

# Articles

## Hyperbranched Nanomolecules: Regular Polystyrene Dendrigrafts

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**ABSTRACT:** Arborescent graft polystyrenes were prepared by the “graft on graft” technique, involving the iterative grafting of end-functional polymer chains onto reactive polymer backbones. The grafts and the reactive backbone building blocks were synthesized individually by living polymerization techniques. The first-generation comb polymers were obtained by the coupling reaction of living  $\alpha$ -acetal polystyryllithium onto poly(chloroethyl vinyl ether) PCEVE chains of controlled  $\overline{DP}_n$ . Initiation from acetal termini of polystyrene branches of a new living cationic polymerization of chloroethyl vinyl ether (CEVE) allowed one to prepare the corresponding comb copolymers with polystyrene-*b*-poly(chloroethyl vinyl ether) branches. Hyperbranched polystyrenes were finally obtained by grafting a second amount of polystyryllithium onto the CEVE units of poly(CEVE) external blocks. Nanomolecules of narrow molar masses distribution, branching functionalities up to 35 000, and molar masses over  $10^8$  g/mol were obtained by this method. By varying  $\overline{DP}_n$  of the different elementary building blocks, various polystyrene dendrigrafts were prepared, demonstrating the possibility to control the core–shell parameters of these macromolecular objects. The solution properties and the characteristic chain parameters ( $[\eta]$ ,  $R_g$ ,  $R_h$ ) of the hyper-branched polystyrene macromolecules were determined and compared with literature data.

### Introduction

In addition to the various random branching reactions that may affect chain architecture in noncontrolled polymerizations, synthetic methods allowing the preparation of specifically highly branched macromolecules have been recently developed.<sup>1–8</sup> Architectures with a single polyfunctional branching point (star polymers) containing arms of the same or different chemical compositions, structures with a given number of branching points distributed randomly or uniformly along a backbone chain (graft and comb polymers),<sup>9–11</sup> and macromolecules possessing regularly distributed “tree-like” or “dendritic” branching points<sup>12–17</sup> (usually called dendrimers) have been prepared and studied, thus covering a broad domain from weakly branched to highly branched architectures.

We have recently reported a new method for the synthesis of monodisperse polystyrene stars and combs with well-controlled chain characteristics (backbone dimensions and architecture and number and size of branches). The method is based on the highly selective coupling of living polystyryllithium onto poly(chloroethyl vinyl ether) chains; both the PS grafts and the poly-(CEVE) building blocks were prepared individually by living polymerizations.<sup>9–11</sup> A similar strategy was very recently applied to the preparation of novel star polymers with four and five comb polystyrene branches.<sup>12</sup> The synthesis of arborescent graft polymers with a dendritic-like architecture, i.e., “dendrigrafts”, using this approach could be of considerable interest since these macromolecules can be obtained in a few steps with a good control of the different structural parameters (number and position of branching points, elementary

polymer segment length). Moreover, such nanometric objects could cover the gap in size between dendrimers and polymer particles.

This paper describes the synthesis of regular PS dendrigrafts from first generation stars and/or comblike polystyrenes and their structural characteristics as well as some of their solution properties.

### Experimental Section

**Materials.** Benzene and toluene (99.5%, J. T. Baker, Deventer, The Netherlands) were purified by distillation over calcium hydride and stored over polystyryllithium seeds.  $\alpha$ -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 (99%, Sigma-Aldrich Chimie, Saint Quentin Fallavier, France) was purified by distillation over calcium hydride at reduced pressure. *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.

HCl gas (99.9% Setec Labo, Versailles, France) was used as received. Zinc chloride (99.999% Sigma-Aldrich Chimie, Saint Quentin Fallavier, France) was dissolved in dry diethyl ether ( $7 \times 10^{-3}$  mol L<sup>-1</sup>).

All the reactants were stored under dry nitrogen in glass apparatus fitted with PTFE stopcocks.

**Techniques.** Because of the high molar masses difference, separation between the graft copolymers (combs and dendrigrafts) and unreacted PS was directly achieved by selective precipitation of the graft structures into a mixture of cyclohexane/heptane (50/50, v/v). In the same way, separation of the comb copolymers (PCEVE<sub>1</sub>-*g*-(PS<sub>1</sub>-*b*-PCEVE<sub>2</sub>) and a small

fraction of linear PCEVE, formed by side initiation involving residual HI, was achieved by selective precipitation of the comb copolymer into diethyl ether/acetone mixture.

SEC measurements were performed in THF at 25 °C (flow rate 0.7 mL/min) on a Varian apparatus equipped with refractive index (Varian) and laser light scattering (Wyatt technology) dual detection and fitted with four TSK gel HXL columns (250, 1500, 10<sup>4</sup>, and 10<sup>5</sup> Å). Calibration in the case of refractive index detection was performed using linear polystyrene or linear poly(CEVE). For light scattering detection, the  $dn/dc$  values of the graft copolymers were determined separately for each type of sample, in THF, with a laser source operating at 633 nm.

<sup>1</sup>H NMR spectra were recorded on a BRUKER AC 200 MHz in CDCl<sub>3</sub>. The  $\overline{DP}_n$  of the poly(CEVE<sub>2</sub>) branches of the comb backbone precursor (PCEVE<sub>1</sub>-*g*-(PS<sub>1</sub>-*b*-PCEVE<sub>2</sub>)) was determined by <sup>1</sup>H NMR from the integration ratio between the units belonging to PS<sub>1</sub> and those of PCEVE blocks considering that the contribution of the central PCEVE<sub>1</sub> backbone is negligible in comparison to the PCEVE<sub>2</sub> blocks.

Dynamic light scattering measurements were performed on a MALVERN apparatus (Zetasizer 3000 HS) equipped with a He-Ne laser source (633 nm). Correlation functions were analyzed by the Contin method. Latex particles were used as calibration standards.

Intrinsic viscosities were measured in THF at 25 °C with an automatized Ubbelohde viscometer (SemaTech).

**Polymerization Procedures. (a) Synthesis of the PS Building Blocks.** The anionic synthesis of polystyryllithium chains using 3-lithiopropionaldehyde diethyl acetal as initiator has been already described.<sup>12</sup>

**(b) Preparation of the Poly(CEVE) (PCEVE) Building Blocks.** For the synthesis of PCEVE<sub>1</sub> (1) used as the central backbone,  $\alpha$ -chloro(2-chloroethyl) ethyl ether, the HCl-CEVE adduct, was used as the chain precursor. Its synthesis and the CEVE polymerization have been already described.<sup>9</sup>

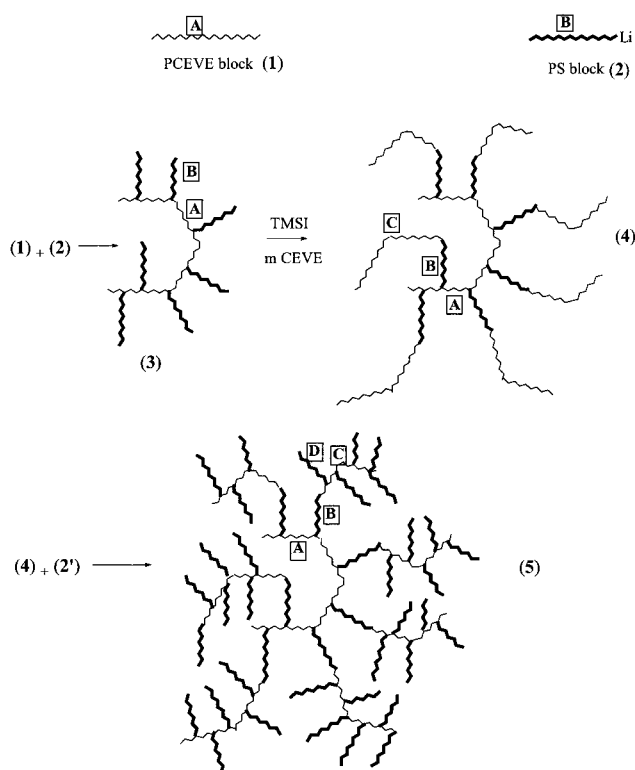
The synthesis of the PCEVE<sub>2</sub> blocks, forming the multi-branched reactive backbone in PCEVE<sub>1</sub>-*g*-(PS<sub>1</sub>-*b*-PCEVE<sub>2</sub>) combs is illustrated in the following example. PCEVE<sub>1</sub>-*g*-PS<sub>1</sub> comb (3) with  $\overline{DP}_n(\text{PCEVE}) = 56$  and  $\overline{DP}_n(\text{PS branch}) = 39$  (20.0 g,  $9.7 \times 10^{-5}$  mol) is placed in a glass reactor fitted with PTFE stopcocks and dissolved in 50 mL of dry toluene. To remove traces of moisture, the solvent was evaporated under vacuum and the polymer was vacuum-dried for 5 h at 60 °C. The operation was repeated twice. The polymer was then redissolved into anhydrous toluene (100 mL) and CEVE (27.0 g,  $25.4 \times 10^{-2}$  mol) was added under nitrogen. The reactor was thermostated at -35 °C and TMSI (1 mL,  $7 \times 10^{-3}$  mol) added to convert acetal end groups of 3 into  $\alpha$ -iodoether ones. After 1 h of stirring at -35 °C, a ZnCl<sub>2</sub> solution (1 mL,  $3 \times 10^{-3}$  g of ZnCl<sub>2</sub>/mL of diethyl ether) was added to initiate the CEVE polymerization and the conversion was followed by SEC analysis of aliquots of the reaction medium. At the end of the polymerization (10 h), a lutidine/methanol solution (10 mL, 1 mol/L) was added to deactivate the polymerization system.

The crude polymer solution was then washed several times with a solution of potassium thiosulfate (50 mL, 2/100 weight) and neutral water. 4 was finally recovered by solvent evaporation under vacuum and characterized (yield 40.5 g,  $\overline{M}_n(\text{RI}) = 1.3 \times 10^5$  g/mol,  $\{\overline{M}_w/\overline{M}_n\} = 1.06$ ).

**(c) Grafting Reactions onto Poly(CEVE).** The preparation of PCEVE<sub>1</sub>-*g*-PS<sub>1</sub> comb structures by termination of PSLi chains onto chloro functions of CEVE units of PCEVE homopolymer as already been described.<sup>10</sup>

Preparation of polystyrene dendrigrafts from PCEVE<sub>1</sub>-*g*-(PS<sub>1</sub>-*b*-PCEVE<sub>2</sub>) combs. A solution of polystyryllithium (8 g PSLi,  $\overline{M}_n = 1590$ ) in benzene (100 mL) was placed in a buret and incrementally added under dry nitrogen atmosphere to comb PCEVE<sub>1</sub>-*g*-(PS<sub>1</sub>-*b*-PCEVE<sub>2</sub>) (respectively  $\overline{DP}_n$  56/39/39, 1 g,  $2.2 \times 10^{-6}$  mol,  $\overline{M}_n = 453\,000$ ), previously degassed under vacuum and dissolved in dry benzene (20 mL). The rate of PSLi addition was determined by the disappearance of the coloration of the PCEVE solution. PSLi was added until a fading pink color of the reacting media remained over about a 24 h period.

Scheme 1



**Table 1. Characteristics and Dimensions of PCEVE Used as Reactive Central backbone (1)**

$\overline{M}(\text{exptl})^a$	$\overline{DP}_n(\text{exptl})^b$	$\overline{M}_w/\overline{M}_n$
2700	26	1.03
3980	36	1.03
6390	56	1.03
81400 <sup>c</sup>	764 <sup>c</sup>	1.03

<sup>a</sup> Apparent peak molar mass determined by SEC using linear polystyrene standards. <sup>b</sup> Determined by proton NMR from the ratio CEVE/terminal acetal. <sup>c</sup> Determined by SEC using linear poly(CEVE) calibration curve.

Deactivation of residual PSLi was finally achieved by adding degassed methanol (1 mL). Yield = 5.5 g,  $\overline{M}_n(\text{SEC}) = 3.3 \times 10^5$ ,  $\overline{M}_n(\text{LS}) = 2.5 \times 10^6$ , and  $\overline{M}_w/\overline{M}_n = 1.1$ .

## Results and Discussion

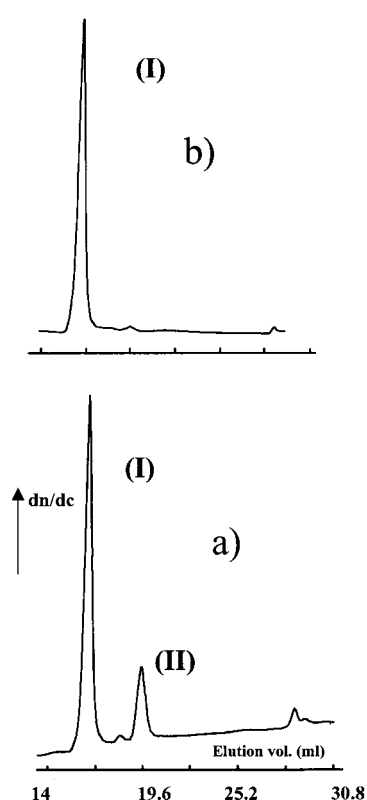
The general approach to the synthesis of PS dendrigrafts is described in Scheme 1. The strategy consists of grafting living polystyryllithium chains (2, 2') onto poly(chloroethyl vinyl ether) chains (PCEVE) of controlled  $\overline{DP}_n$ . Polystyryllithium grafts were prepared in benzene in the presence of a equimolar amount of tetramethyl ethylenediamine (TMEDA), using propyl-lithium diethylacetal as the initiating system.<sup>12</sup> PCEVE<sub>1</sub> homopolymers (1) were prepared as previously described by living cationic polymerization and were used as precursors for the preparation of first generation branched macromolecules (Scheme 2). The grafting reaction of anionic PSLi chains was performed by adding the living carbanionic solutions onto a known quantity of PCEVE, until a persistent light-red coloration of the medium remained.

The high selectivity of the reaction between carbanionic chain ends and chloroethyl ether groups has been recently demonstrated in the synthesis of series of poly-(chloroethyl vinyl ether)-*g*-polystyrene stars<sup>9</sup> as well as

**Table 2. Characteristics of PCEVE<sub>1</sub>-g-PS<sub>1</sub> Comblike Polymers**

comb ref	PCEVE <sub>1</sub> DP <sub>n</sub>	PSLi <sub>1</sub>		comb polymer				$\bar{f}^d$	$\eta$ (dL/g) <sup>e</sup>
		$\bar{M}_n(\text{exptl})^a$	$\bar{M}_n(\text{theor})^b$	$\bar{M}_n \text{ RI}^a$	$\bar{M}_w \text{ LS}^c$	$\bar{M}_w/\bar{M}_n$			
26/150	26	$1.52 \times 10^4$	$3.95 \times 10^5$	$1.27 \times 10^5$	$4.00 \times 10^5$	1.07		25	0.19
26/51	26	$5.30 \times 10^3$	$1.40 \times 10^5$	$6.00 \times 10^4$	$1.64 \times 10^5$	1.06		30	0.12
36/180	36	$1.92 \times 10^4$	$6.93 \times 10^5$	$1.93 \times 10^5$	$7.22 \times 10^5$	1.05		36	0.20
56/39	56	$3.93 \times 10^3$	$2.20 \times 10^5$	$7.11 \times 10^4$	$2.07 \times 10^5$	1.06		53	
56/31	56	$3.22 \times 10^3$	$1.80 \times 10^5$	$5.50 \times 10^4$	$1.62 \times 10^5$	1.15		51	0.09
764/81	764	$8.50 \times 10^3$	$6.50 \times 10^6$	$9.90 \times 10^5$	$5.80 \times 10^6$	1.06		637	0.46

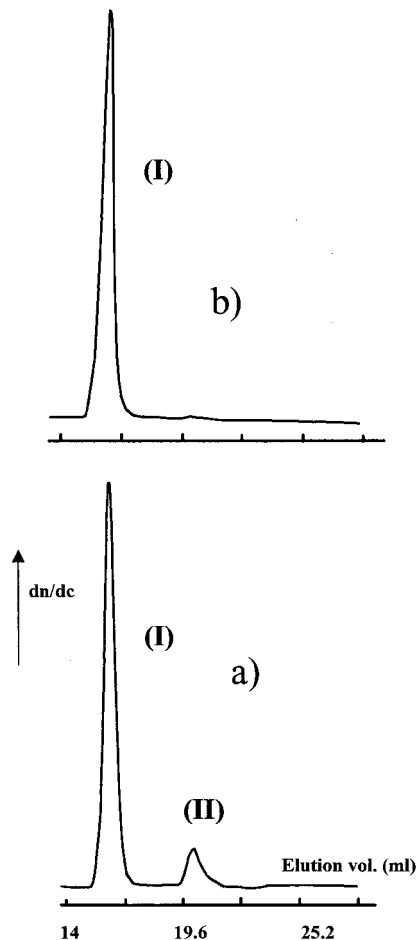
<sup>a</sup> Determined by SEC using linear PS as calibration standards. <sup>b</sup> Calculated from  $\overline{\text{DP}}_n \text{PCEVE}_1 \times \overline{M}_n \text{PS}_1$ . <sup>c</sup> Determined by SEC using light scattering detector with  $dn/dc = 0.77$  in THF at 25 °C. <sup>d</sup> Number of branches estimated from the ratio  $\bar{M}_w$  (LS) comb polymer/ $\bar{M}_n$  PS branch. <sup>e</sup> THF, 25 °C.



**Figure 1.** SEC chromatograms of PCEVE<sub>1</sub>-g-PS<sub>1</sub> comb (3) (I,  $\overline{\text{DP}}_n = 26/150$ ): (a) crude products; (b) products after fractionation and elimination of the unreacted PS<sub>1</sub> (II).

of both linear and cyclic comb copolymers.<sup>10</sup> High efficiency in the substitution reaction of chloride was used to get starlike and comblike polymers with a uniform number of branches.<sup>9</sup>

In the present work, this methodology was first applied to the synthesis of regular branched comblike polystyrenes having a controlled number of  $\omega$ -acetal-PS branches of same length attached to a linear PCEVE<sub>1</sub> backbone, see Table 1. The SEC chromatogram of a typical crude poly(chloroethyl vinyl ether)-g-polystyrene graft copolymer ( $\overline{\text{DP}}_{n(\text{PCEVE})} = 26$ ,  $\overline{M}_{n\text{PSgraft}} = 150$ ) is presented in Figure 1. The main signal (I), located in the high molar mass domain, corresponds to the graft copolymer. Population II, with  $\bar{M}_n$  identical to that of the initial PSLi, corresponds to the excess of PSLi added. This fraction was easily removed by selective precipitation of I into cyclohexane/hexane mixtures. The characteristics of the corresponding PCEVE<sub>1</sub>-g-PS<sub>1</sub> graft copolymers (3) are collected in Table 2. The theoretical molar masses of the graft copolymers calculated from



**Figure 2.** SEC chromatograms of PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-PCEVE<sub>2</sub>) comb copolymer (4) (I,  $\overline{\text{DP}}_n = 26/150/50$ ): (a) crude products; (b) products after fractionation and elimination of the homo PCEVE<sub>2</sub> (II).

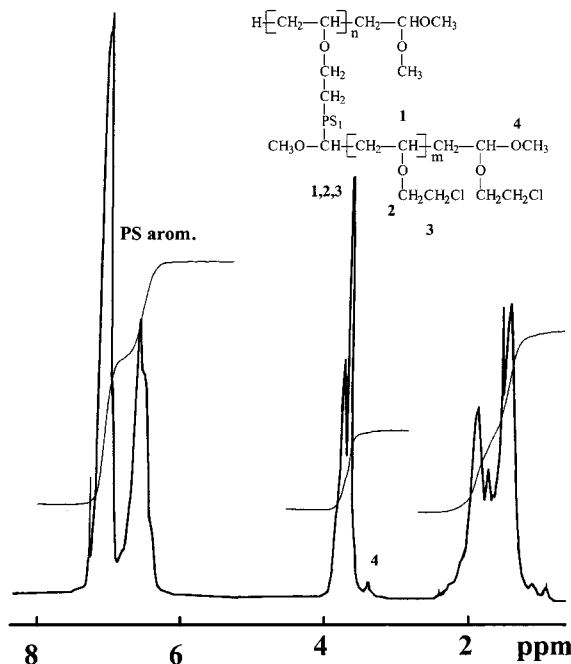
the molar mass of the PCEVE<sub>1</sub> backbone and that of the PS<sub>1</sub> graft, assuming one graft per CEVE unit, closely fit with experimental molar masses determined by SEC using light scattering detection. Data confirm that grafting is quantitative with respect to the chloroether functions.

**Preparation of PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-PCEVE<sub>2</sub>) Comb Copolymers (4).** The living/controlled character of the cationic chloroethyl vinyl ether polymerization was further used to grow PCEVE blocks from the macromolecular chain precursor (3). Initiation of the CEVE polymerization from the acetal end of polystyrene branches was performed as previously described by adding to the branched macromolecular precursor solution successively trimethylsilyl iodide (TMSI), the monomer, and zinc chloride as catalyst.<sup>19</sup> A typical SEC

**Table 3. Characteristics of PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-PCEVE<sub>2</sub>) Comblike Copolymers**

polymer ref	PCEVE <sub>1</sub> $\overline{DP}_n$	PS <sub>1</sub> $\overline{M}_n$ (exptl) <sup>a</sup>	comb copolymer			
			PCEVE <sub>2</sub> <sup>b</sup> $\overline{DP}_n$	$\overline{M}_n$ RI <sup>a</sup>	$\overline{M}_n$ ex <sup>b</sup>	$\overline{M}_w/\overline{M}_n$
26/150/50	26	$1.5 \times 10^4$	50	$1.60 \times 10^5$	$5.34 \times 10^5$	1.07
26/51/82	26	$5.3 \times 10^3$	82	$1.24 \times 10^5$	$3.65 \times 10^5$	1.06
36/180/67	36	$1.9 \times 10^4$	67	$3.05 \times 10^5$	$9.48 \times 10^5$	1.05
56/39/39	56	$3.9 \times 10^3$	39	$1.31 \times 10^5$	$4.53 \times 10^5$	1.06
56/31/21	56	$3.2 \times 10^3$	21	$9.74 \times 10^4$	$3.04 \times 10^5$	1.12
764/81/50	764	$8.5 \times 10^3$	50	$1.50 \times 10^6$	$10.50 \times 10^6$	1.06

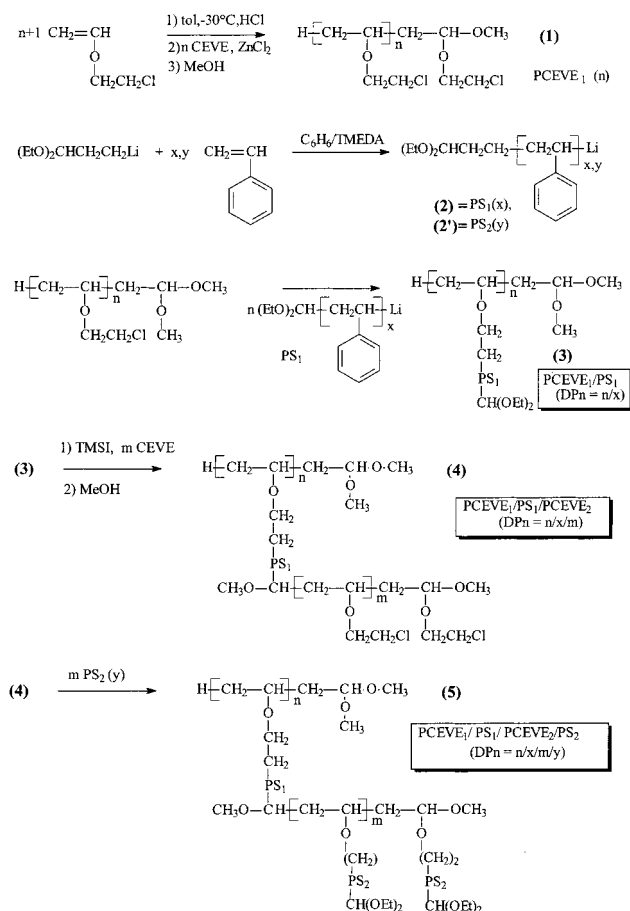
<sup>a</sup> Determined by SEC using linear PS as calibration standards. <sup>b</sup>  $\overline{DP}_n$  determined by proton NMR from the ratio CEVE units/S units after fractionation.



**Figure 3.** <sup>1</sup>H NMR spectrum and peak assignments of PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-PCEVE<sub>2</sub>) comb copolymer (**4**) ( $\overline{DP}_n$  = 26/150/50).

chromatogram of a PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-PCEVE<sub>2</sub>) comblike copolymer is presented in Figure 2. The main signal (I) located in the high molar mass domain corresponds to the branched copolymer. Peak II indicates the formation of some linear homo PCEVE chains due to side initiation involving reaction of TMSI with traces of water. This low molar mass fraction was easily removed by selective precipitation of **4** in acetone/diethyl ether mixture (Figure 2b). The total number of CEVE units per macromolecule was determined by <sup>1</sup>H NMR from the relative integrals of CEVE units/styrene units of the precursor (**3**), Figure 3. We have shown in a previous study that CEVE initiation from acetal chain termini is a quantitative reaction.<sup>12</sup> The comb molar mass increase, as determined by SEC using light scattering detection, and the narrow dispersity of the branched block copolymers ( $I_p \leq 1.1$ ) are in good agreement with an homogeneous growth of PCEVE blocks at almost each polystyrene branch end and support the good control of the grafting from process. The dimensional characteristics of the corresponding PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-PCEVE<sub>2</sub>) comb copolymers (**4**) are collected in Table 3.

**Polystyrene Dendrigrafts (5).** Their preparation was finally achieved by grafting PSLi chains (**2'**) onto the PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-PCEVE<sub>2</sub>) combs (**4**), Scheme 2. As previously indicated, due to the large difference in their molar masses, the hyper-ramified structure could be

**Scheme 2**

easily separated from ungrafted polystyrene PS<sub>2</sub> by selective precipitation in a cyclohexane/*n*-heptane mixture. Figure 4 shows the SEC of the hyper-branched copolymer obtained from PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-PCEVE<sub>2</sub>) with blocks of respective  $\overline{DP}$ , 26/150/50 and final PS<sub>2</sub> graft of  $\overline{DP}_n$  = 50. The peak is unimodal and remains quite narrow ( $\leq 1.1$ ) which is consistent with a clean and homogeneous grafting process.

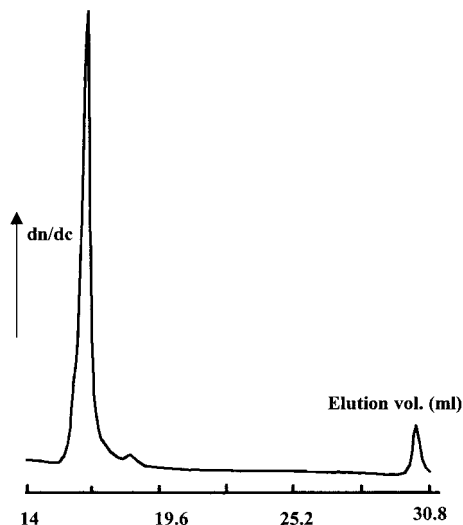
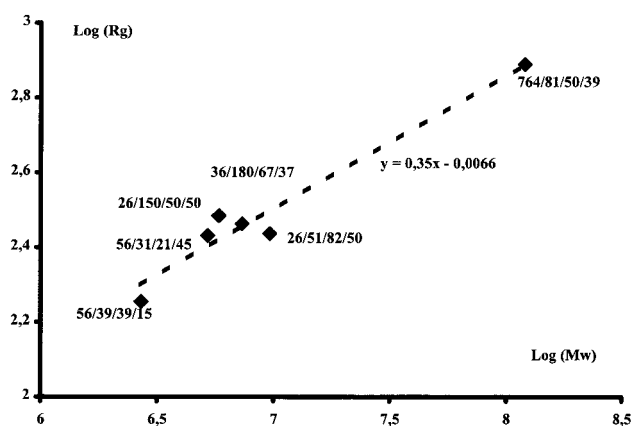
The dimensional and solution characteristics of several hyper-branched structures are collected in Table 4. The theoretical molar masses of the PS dendrigrafts, calculated from the  $\overline{DP}_n$  of the poly(CEVE) backbone (**4**) and the  $\overline{M}_n$  of the PS<sub>2</sub> graft, assuming one graft per CEVE unit, agree with the experimental molar masses determined by SEC using light scattering detection, and the molar masses distributions remain narrow ( $\overline{M}_w/\overline{M}_n < 1.3$ ) for each dendrigraft. Molar masses up to 100 million were measured for these polymers of the second generation.



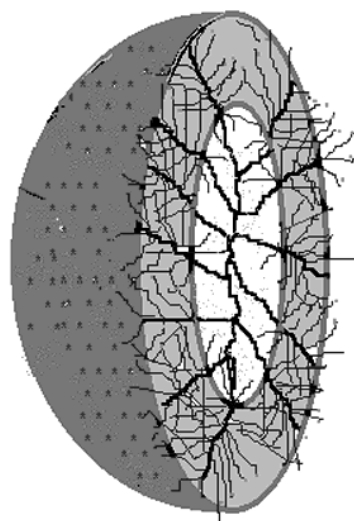
**Table 4. Characteristics of PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-(PCEVE<sub>2</sub>-g-PS<sub>2</sub>)) Dendrigrfts**

samples $\overline{DP}_n$ of elementary blocks	PS <sub>2</sub> $\bar{M}_n(\text{exptl})^a$	dendrigrft								
		RI detector <sup>a</sup>		LS detector <sup>a</sup>		$R_g$ (nm)	$[\eta]^c$ (dL/g)	$R_h$ (nm)	$R_{\eta}^d$ (nm)	$d$ (g/cm <sup>3</sup> )
		$\bar{M}_n(\text{theor})^b$ (g/mol)	$\bar{M}_n(\text{exptl})$ (g/mol)	$\bar{M}_w(\text{exptl})$ (g/mol)	$\bar{M}_n(\text{exptl})$ (g/mol)					
26/150/50/50	5440	$7.7 \times 10^6$	$7.0 \times 10^5$	$5.8 \times 10^6$	$5.0 \times 10^6$	30.5	0.26	28	27	0.12
26/51/82/50	5400	$11.0 \times 10^6$	$3.1 \times 10^5$	$9.6 \times 10^6$	$9.4 \times 10^6$	27.3	0.13	21	27	0.19
36/180/67/37	3800	$7.9 \times 10^6$	$7.2 \times 10^5$	$7.3 \times 10^6$	$6.9 \times 10^6$	29	0.25	27	30	0.11
56/39/39/15	1590	$3.5 \times 10^6$	$3.3 \times 10^5$	$2.7 \times 10^6$	$2.5 \times 10^6$	18		17		
56/31/21/45	4700	$5.7 \times 10^6$	$6.7 \times 10^5$	$5.2 \times 10^6$	$5.0 \times 10^6$	27	0.12		21	0.22
764/81/50/39	4060	$1.5 \times 10^8$	$3.1 \times 10^6$	$1.3 \times 10^8$	$1.2 \times 10^8$	77.5	0.19	60	71	0.13

<sup>a</sup>  $\bar{M}_n$  and  $\bar{M}_w$  determined by SEC using refractive index (RI) or light scattering (LS) detectors;  $dn/dc = 0.177$  in THF at 25 °C. <sup>b</sup>  $\bar{M}_n$  Calculated from  $\overline{DP}_n \text{PCEVE}_1[\bar{M}_n \text{PS}_1 + (\overline{DP}_n \text{PCEVE}_2 \times \bar{M}_n \text{PS}_2)]$ . <sup>c</sup> Viscosity measured in THF at 25 °C. <sup>d</sup> Calculated from the Einstein equation.

**Figure 4.** SEC chromatograms of PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-(PCEVE<sub>2</sub>-g-PS<sub>2</sub>)) dendrigrft (5) ( $\overline{DP}_n = 26/150/50/50$ ) after elimination of the excess PS<sub>2</sub> by selective reprecipitation.**Figure 5.** Double logarithmic variation of  $R_g$  with the experimental molar mass of PCEVE<sub>1</sub>-g-(PS<sub>1</sub>-b-(PCEVE<sub>2</sub>-g-PS<sub>2</sub>)) dendrigrfts.

By treating the logarithm of radius of gyration against the logarithm of experimental weight average molar mass, it is found that its size ( $R_g$ ) fits approximately the relation  $R_g \propto M^\nu$  with  $\nu = 0.35$ , Figure 5. This value of the exponent is consistent with the theoretical prediction of De Gennes and Harvet<sup>21</sup> ( $\nu = 0.2-0.3$ ) and Murat and Grest<sup>22</sup> ( $\nu = 0.33$ ) for classical dendrimers. These results suggest that most of the hyperbranched polymers have a spherical shape. However, when examining more carefully data for samples in the lower molar mass

**Scheme 3**

range, the agreement is questionable. This can be explained by the complex chain architecture of these macromolecular objects which is characterized, in addition to the molar mass, by four independent chain parameters corresponding successively to the dimensions of the PCEVE backbone, the first PS graft, the second PCEVE block and the final PS graft. Change in one of these parameters yield different families of hyperbranched polymers for which  $k$  and  $\nu$  can differ in the equation  $R_g = kM^\nu$ . Moreover, experimental evidences, obtained in the solution and in the bulk, respectively, by neutron scattering<sup>23</sup> and AFM,<sup>24</sup> show that depending on the main backbone length (PCEVE<sub>1</sub>) the shape of the nanomolecules may vary from spherical to cylindrical. This last topology is clearly observed for the sample with a PCEVE backbone of  $\overline{DP}_n = 764$ .

Indeed, regarding the different chain building parameters, it is believed that the  $\overline{DP}_n$  of the PCEVE backbone that determine the number of first PS grafts will contribute to the shape of the object which can then varies from spherical to rodlike.<sup>24</sup> The first generation of PS branches can be considered mostly as a spacer bearing the second-generation building blocks constituting the shell of the object.  $\overline{DP}_n$  of the outer PCEVE blocks will determine the potential number of external PS grafts per branch and therefore will contribute to the shell thickness. This last parameter is also determined by the molar mass of the outer PS graft. In the different reported examples, Table 4, this last block

**Table 5. Comparison of the Radius of Gyration ( $R_g$ ) and the Density of Linear, Comb, and Dendrigrraft Polystyrenes in THF Solution at 25 °C (Molar Mass of the Polymer:  $7 \times 10^6$  g/mol)**

	linear PS <sup>a</sup>	PS comb	PS dendrigrraft
$\langle R_g \rangle$ (nm)	133.8	34.2	25
density (g/cm <sup>3</sup> )	$1.2 \times 10^{-3}$	$6.9 \times 10^{-2}$	$1.8 \times 10^{-1}$

<sup>a</sup> Calculation based on data given in ref 18 in the case of a polymer of molar mass of  $7 \times 10^6$  g/mol.

represents more than 95% percent of the total mass of the unimolecular particle.

Viscosity measurements performed in THF and cyclohexane confirms that the PS dendrigrrafts behave as compact nondraining spheres or cylinders, as previously reported for other hyperbranched polystyrene structure.<sup>18–20</sup> Intrinsic viscosities are lowered by about a factor  $10^2$  in comparison with linear polystyrene of same molar mass. Indeed, no noticeable solvent effect on the particle dimensions is observed when going from good to a  $\Theta$  solvent. Interestingly, the viscosity and the dimensions of the particles, the viscosimetric radius ( $R_\eta$ ) and the hydrodynamic radius ( $R_h$ ) are significantly affected by the length of the PS<sub>1</sub> blocks. For dendrigrrafts of about the same molar mass, the higher the PS<sub>1</sub> DP<sub>n</sub>, the higher the viscosity and the dimensions of the particle. For example, sample 26/150/50/50 ( $\overline{M}_w \text{exp}_{LS} = 5.8 \times 10^6$  g/mol), exhibits  $[\eta]$ ,  $R_\eta$  and  $R_h$  about two times higher than the 26/51/82/50 sample of higher molar mass ( $\overline{M}_w \text{exp}_{LS} = 9.8 \times 10^6$  g/mol). This is consistent with a strong extension of the PS<sub>1</sub> segments, thus yielding to the formation of an empty space inside the particle, see Scheme 3. Monomer unit density in the particles in solution was estimated from their gyration radius and molar masses. In a good solvent, calculation indicates that the number of styrene units by arbitrary volume unit is approximately 200 times higher than that for linear polymers yet 3–4 times higher than that for polystyrene combs, in agreement with the high compactness of these unimolecular particles; see Table 5.

In conclusion, a new strategy for the synthesis in a few steps of unimolecular nanoparticles based on covalent assembly of elementary macromolecular blocks has been developed. The possibility to adjust the structure and dimensions of the different building elements all prepared by living polymerization techniques allows a good control of the size, shape, compactness and functionality of the final objects. This opens interesting

possibilities in tuning their properties for specific applications such as host–guest interactions in the presence of organic molecules.

Functionalization of the particle surface by hydrophilic groups and their impact on the solubility and solution properties of the dendrigrrafts will be reported in a forthcoming publication.

## References and Notes

- (1) Branched Polymers I and II. In *Advances in Polymer Science*; Roovers, J., Vol. Ed.; Springer-Verlag: Berlin 1999; Vols. 142 and 143.
- (2) Star and hyperbranched Polymers. In *Plastics Engineering Series*; Mishra, M. K., Kobayashi, S., Eds.; Marcel Dekker, Inc.: New York 1999; Vol. 53.
- (3) Hempenius, M. A.; Michelberger, W.; Moller, M. *Macromolecules* **1997**, *30*, 5602, 17.
- (4) Roovers, J. *Encycl. Polym. Sci. Eng.* **1985**, *2*, 478.
- (5) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138.
- (6) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Frechet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401.
- (7) Voit, B. J. *Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505.
- (8) Haag, R. *Chem. Eur. J.* **2001**, *7*, 327.
- (9) Deffieux, A.; Schappacher, M. *Macromolecules* **1999**, *32*, 1797.
- (10) Schappacher, M.; Billaud, C.; Paulo, C.; Deffieux, A. *Makromol. Chem. Phys.* **1999**, *200*, 2377.
- (11) Schappacher, M.; Deffieux, A. *Makromol. Chem. Phys.* **1997**, *198*, 3953.
- (12) Deffieux, A.; Schappacher, M. *Macromol. Symp.* **1998**, *132*, 45. Schappacher, M.; Deffieux, A. *Macromolecules* **2000**, *33*, 7371.
- (13) Choi, S.; Briber, R. M.; Bauer, B. J.; Topp, A.; Gauthier, M.; Tichagwa, L. *Macromolecules* **1999**, *32*, 7879, 18.
- (14) Gauthier, M.; Moller, M. *Macromolecules* **1991**, *24*, 4548.
- (15) Gauthier, M.; Tichagwa, L.; Downey, J. S.; Gao, S. *Macromolecules* **1996**, *29*, 519. Choi, S.; Briber, R. M.; Bauer, B. J.; Liu, D.; Gauthier, M. *Macromolecules* **2000**, *33*, 6495.
- (16) Sheiko, S. S.; Gauthier, M.; Moller, M. *Macromolecules* **1997**, *30*, 2343.
- (17) Choi, S.; Briber, R. M.; Bauer, B. J.; Topp, A.; Gauthier, M.; Tichagwa, L. *Macromolecules* **1996**, *29*, 519.
- (18) Wintermantel, M.; Gerle, M.; Fischer, K.; Schmidt, M.; Wataoka, I.; Urakawa, K.; Tsukahara, Y. *Macromolecules* **1996**, *29*, 978.
- (19) Schappacher, M.; Deffieux, A.; Haucourt, N.; Goethals, E. *Makromol. Chem. Rapid. Commun.* **1992**, *13*, 329.
- (20) Striolo, J. M.; Praunitz, J. M.; Bertuccio, A.; Kee, R. A.; Gauthier, M. *Polymer* **2001**, *42*, 2579.
- (21) De Gennes; P.-G.; Hervet, H. *J. Phys. Lett.* **1983**, *44*, L351.
- (22) Murat, M.; Grest, G. S. *Macromolecules* **1996**, *29*, 1278.
- (23) Borsali, R.; Lecommandoux S.; Schappacher, M.; Deffieux, A. Manuscript in preparation.
- (24) Viville, P.; Deffieux, A.; Schappacher, M.; Bredas, J. L.; Lazzaroni, R. *Makromol. Symp.* **2001**, *167*, 243.

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