

# New Polymer Chain Architecture: Synthesis and Characterization of Star Polymers with Comb Polystyrene Branches

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**ABSTRACT:** Highly branched starlike comb polystyrenes (star polymers with four and five arms constituted of PS combs) have been synthesized. The strategy developed is based on the highly selective coupling reaction of living polystyryllithium onto poly(chloroethyl vinyl ether) chains with a starlike chain architecture. The PS grafts and the poly(CEVE) building blocks were prepared individually by living polymerization techniques. The solution properties and the characteristic parameters ( $[\eta]$ ,  $R_g$ ,  $R_h$ ,  $\rho$ ) of these new PS comb star macromolecules were determined and compared to those of the corresponding "linear" PS combs. The results confirm the much higher compactness of the new macromolecular structures, which behave as hard spheres in the whole molar mass domain examined.

## Introduction

The synthesis and study of the solution and bulk properties of polymers with nonlinear chains has received considerable attention in the past decade. Among these materials, branched polymers<sup>1,2</sup> constitute an extremely diversified group. In addition to the random branching that occurs in noncontrolled polymerizations, synthetic methods allowing highly specific branching have been developed. 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), and macromolecules possessing regularly distributed "treelike" or "dendritic" branching points (usually called dendrimers) have been prepared and studied, thus covering a broad domain from weakly branched to hyperbranched architectures.

The chain architecture drastically influences the polymer properties in many cases. Tentative interpretations and theories have been proposed; however, for a general understanding of these effects, model polymers with well-defined chain topology, controlled molar masses, and narrow molar mass distributions should be studied.

Model polymers with controlled chain parameters and topologies of increasing complexity must be synthesized by living or controlled polymerization reactions and highly selective polymer functionalization and coupling reactions.

We have recently reported 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>3–6</sup>

This paper reports the application of this methodology to the synthesis of highly branched starlike comb polystyrenes; ie star polymers with arms constituted of

PS combs. The specific characteristics and solution properties of the new star PS combs are described and compared to those of the corresponding "linear" PS combs.

## 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% Setic 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.** <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) branches of the star backbone precursor <sup>*r*</sup>(PCEVE) was determined by <sup>1</sup>H NMR from the integration ratio between the units belonging to PS<sub>1</sub> blocks and to poly(CEVE) blocks and by light scattering.

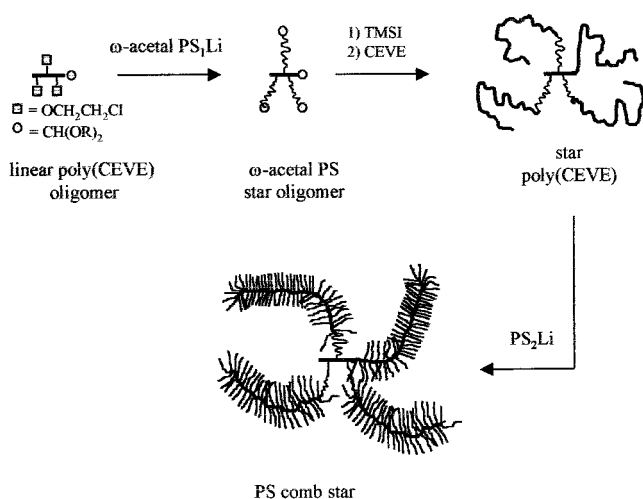
HPLC fractionation was achieved on a JASCO apparatus PU987 equipped with a RI detector and fitted with a semi-preparative silica column (Spherisorb S5W, 280 × 20 mm). The crude poly(CEVE) oligomers (<sup>*1*</sup>)<sub>n</sub> ( $\overline{DP}_n = 6$ ) was fractionated into a series of isometric fractions (<sup>*1*</sup>)<sub>x</sub> as indicated in ref 3. The poly(CEVE)-*g*-PS<sub>1</sub> precursors (<sup>*2*</sup>) and the star copolymers (<sup>*4*</sup>(PCEVE)) were freed respectively from unreacted or dimerized PS<sub>1</sub> oligomers and from linear PCEVE oligomers using a THF/heptane mixture (60/40 v/v) as eluent.

Because of the high molar masses difference, separation between the comb star copolymers <sup>*r*</sup>(PCEVE-*g*-PS<sub>2</sub>) and unreacted PS<sub>2</sub> was much easier and was directly achieved by selective precipitation of the comb star into a mixture of cyclohexane/heptane (50/50, v/v).

SEC measurements were performed in THF at 25 °C (flow rate 1 mL/min) on a Varian apparatus equipped with refractive index (Varian) and laser light scattering (Wyatt technology)

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Scheme 1



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  $dn/dc$  of the graft copolymers was determined separately for each type of samples, in THF, with a laser source operating at 633 nm.

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 *sec*-butyllithium or 3-lithiopropionaldehyde diethyl acetal as initiator has been already described.<sup>7</sup>

**(b) Preparation of the Poly(CEVE) Building Blocks.** For the synthesis of poly(CEVE) oligomers ( $1$ )<sub>*n*+1</sub> used as central backbone,  $\alpha$ -chloro(2-chloroethyl) ethyl ether, the HCl–CEVE adduct, was used as chain precursor. Its synthesis and the CEVE polymerization have been already described.<sup>3</sup> The chloroethoxy-methoxy acetal end of poly(CEVE) oligomers ( $1$ )<sub>*n*+1</sub>, was converted into a dimethoxy acetal terminus by treatment of the polymer with acidic methanol for 4 h in methylene dichloride at 20 °C to yield ( $1'$ )<sub>*n*</sub>.

The synthesis of the second type of poly(CEVE) blocks forming the multibranch backbone is illustrated in the following example. Oligomer  $^3(2')$  (2.0 g,  $2.2 \times 10^{-4}$  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 oligomer was vacuum-dried for 1 h at 60 °C. The operation was repeated twice. The oligomer was then redissolved into anhydrous toluene (100 mL) and CEVE (12.0 g,  $11.3 \times 10^{-2}$  mol) was added under nitrogen. The reactor was thermostated at –35 °C and TMSI (0.14 mL,  $0.99 \times 10^{-3}$  mol), added to convert acetal end groups of structure  $^3(2')$ , 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 polymer solution was then washed several times with a solution of potassium thiosulfate (50 mL, 2/100 weight) and neutral water.  $^4(\text{PCEVE})$  was finally recovered by solvent evaporation under vacuum and characterized (yield 13.5 g,  $\bar{M}_{n,RI} = 3.1 \times 10^5$  g/mol,  $\bar{M}_w/\bar{M}_n = 1.06$ ).

**(c) Preparation of Star Poly(CEVE)-*g*-polystyrene Copolymers: Grafting Reactions.** A solution of polystyryllithium (5 g PSLi 3100) in benzene (100 mL) was placed in a buret and incrementally added under dry nitrogen atmosphere to starlike  $^4(\text{PCEVE})$  poly(chloroethyl vinyl ether) (0.1 g,  $1.8 \times 10^{-6}$  mol,  $\bar{M}_n = 53\,800$ ), 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 poly(CEVE) solution. PSLi was added until a fading pink color of the reacting media remained over about a 24 h period. Residual PSLi was finally deactivated by adding degassed methanol (1 mL). Yield = 2.9 g,  $\bar{M}_{n,SEC} = 0.31 \times 10^6$ ,  $\bar{M}_{n,LS} = 1.42 \times 10^6$ , and  $\bar{M}_w/\bar{M}_n = 1.06$ .

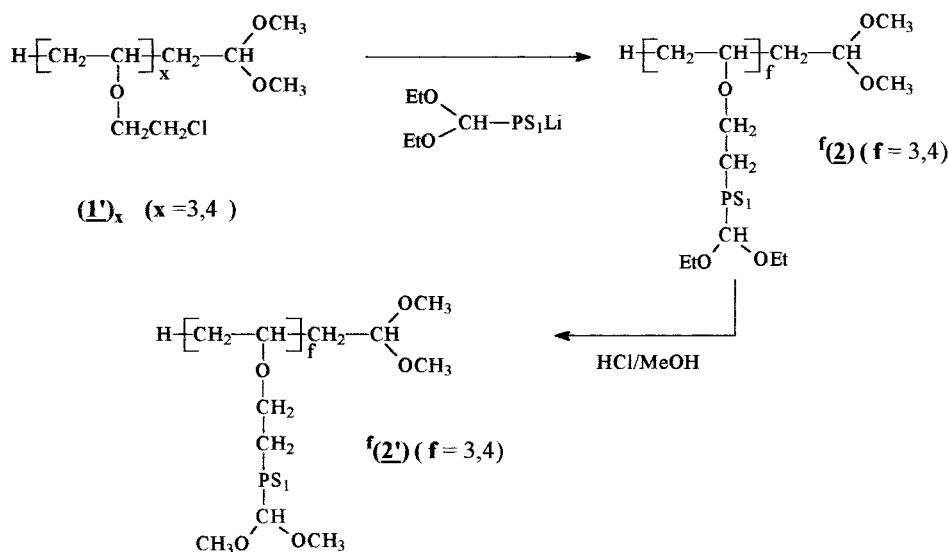
## Results and Discussion

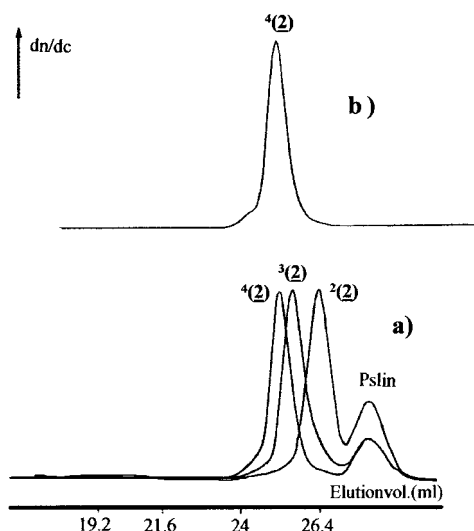
The synthesis of the hyperbranched star polymers with comb polystyrene arms is illustrated in Scheme 1 for a star with four PS comb branches. Starlike poly(chloroethyl vinyl ether)s prepared from plurifunctional oligomer precursors are used as reactive backbones for grafting polystyrene chains. PS grafting is achieved by deactivation of living polystyryllithium chains onto the chloroethyl ether group of the CEVE units as already described.<sup>3</sup>

The different building steps yielding tetrapod (and pentapod) comblike polystyrenes will be successively examined in the following sections.

### 1. Synthesis of Plurifunctional Polymerization Precursors Based on Poly(CEVE) Oligomers. The

Scheme 2



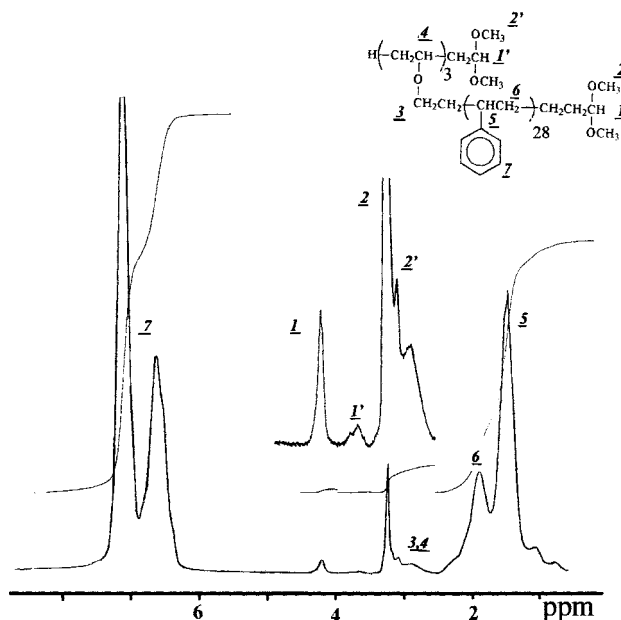


**Figure 1.** SEC chromatograms of  $\omega$ -dimethoxy acetal poly(CEVE)- $g$ - $\alpha$ -dimethoxy acetal PS<sub>1</sub>: (a) crude reaction products <sup>2</sup>(2), <sup>3</sup>(2), and <sup>4</sup>(2); (b) purified fraction <sup>4</sup>(2).

synthesis of plurifunctional oligomers used as cationic initiator in the preparation of multibranch poly(CEVE) is summarized in Scheme 2. It relies in a preliminary step on the preparation of poly(CEVE) oligomers, (<sup>1</sup>)<sub>*n*</sub> which are then fractionated into isometric oligomers by preparative HPLC. The procedure has been described in detail in a previous paper.<sup>3</sup> Three pure fractions (<sup>1</sup>)<sub>*x*</sub> denoted (<sup>1</sup>)<sub>2</sub>, (<sup>1</sup>)<sub>3</sub>, and (<sup>1</sup>)<sub>4</sub>, constituted respectively of oligomers with 2, 3, and 4 CEVE units, were obtained and used as such.

Plurifunctional cationic chain initiators were obtained in a second step by grafting  $\alpha$ -diethoxy acetal polystyryllithium oligomers, PS<sub>1</sub>Li, onto the chloroethyl functions of poly(CEVE) isometric fractions (<sup>1</sup>)<sub>3</sub> and (<sup>1</sup>)<sub>4</sub>, Scheme 2. The PS<sub>1</sub> grafts ( $\bar{M}_n = 2900$ ) were prepared by living anionic polymerization of styrene initiated by lithium diethoxy propyl acetal in order to introduce an acetal group at the end of the polystyrene chain.<sup>7</sup> Grafting was then performed by slowly adding an excess of the PSLi solution (about 1.1–1.2:1 equiv), onto the poly(CEVE) oligomers in benzene,<sup>3</sup> until there was a persistent light red color.

The poly(CEVE)- $g$ -PS graft polymers, were then separated from ungrafted PS by preparative HPLC. The SEC chromatograms of the corresponding graft polymers denoted <sup>3</sup>(2) and <sup>4</sup>(2), in which the number of branches is indicated by the exponent, are presented in Figure 1. The  $\omega$ -diethoxy acetal group of the PS<sub>1</sub>



**Figure 2.** <sup>1</sup>H NMR spectrum and peak assignments of  $\omega$ -dimethoxy acetal poly(CEVE)- $g$ - $\alpha$ -dimethoxy acetal PS<sub>1</sub> graft polymer <sup>3</sup>(2).

branches was converted into a dimethoxy acetal one using acidic methanol, to yield  $\omega$ -dimethoxy poly(CEVE)- $g$ - $\omega$ -dimethoxy acetal PS<sub>1</sub>, with three <sup>3</sup>(2') and four <sup>4</sup>(2') polystyrene arms (Scheme 2). The copolymer structure and the exact number of PS arms per poly(CEVE) chain was confirmed by <sup>1</sup>H NMR. The spectrum of <sup>3</sup>(2') is presented in Figure 2. The characteristics and dimensions of poly(CEVE)- $g$ - $\omega$ -dimethoxy acetal PS<sub>1</sub> with three and four branches are given in Table 1. As expected for branched architectures, the apparent SEC molar masses (relative to linear PS) are much lower than the theoretical values calculated assuming one PS graft per CEVE unit. Indeed, the ratio  $\bar{M}_{n \text{ app}}^{\text{SEC}}/\bar{M}_{n \text{ star th}}$  closely follows the empirical relationship between the number of branches  $f$  of star polymers and the contraction factor,  $g = [(3f - 2)/f^2]$ . In both the present and previous<sup>3</sup> cases,  $\bar{M}_{n \text{ app}}/\bar{M}_{n \text{ star}} = g^{0.43}$ . Theoretical calculation of the degree of branching of star polymers using the expression developed by Liu et al.<sup>9</sup>

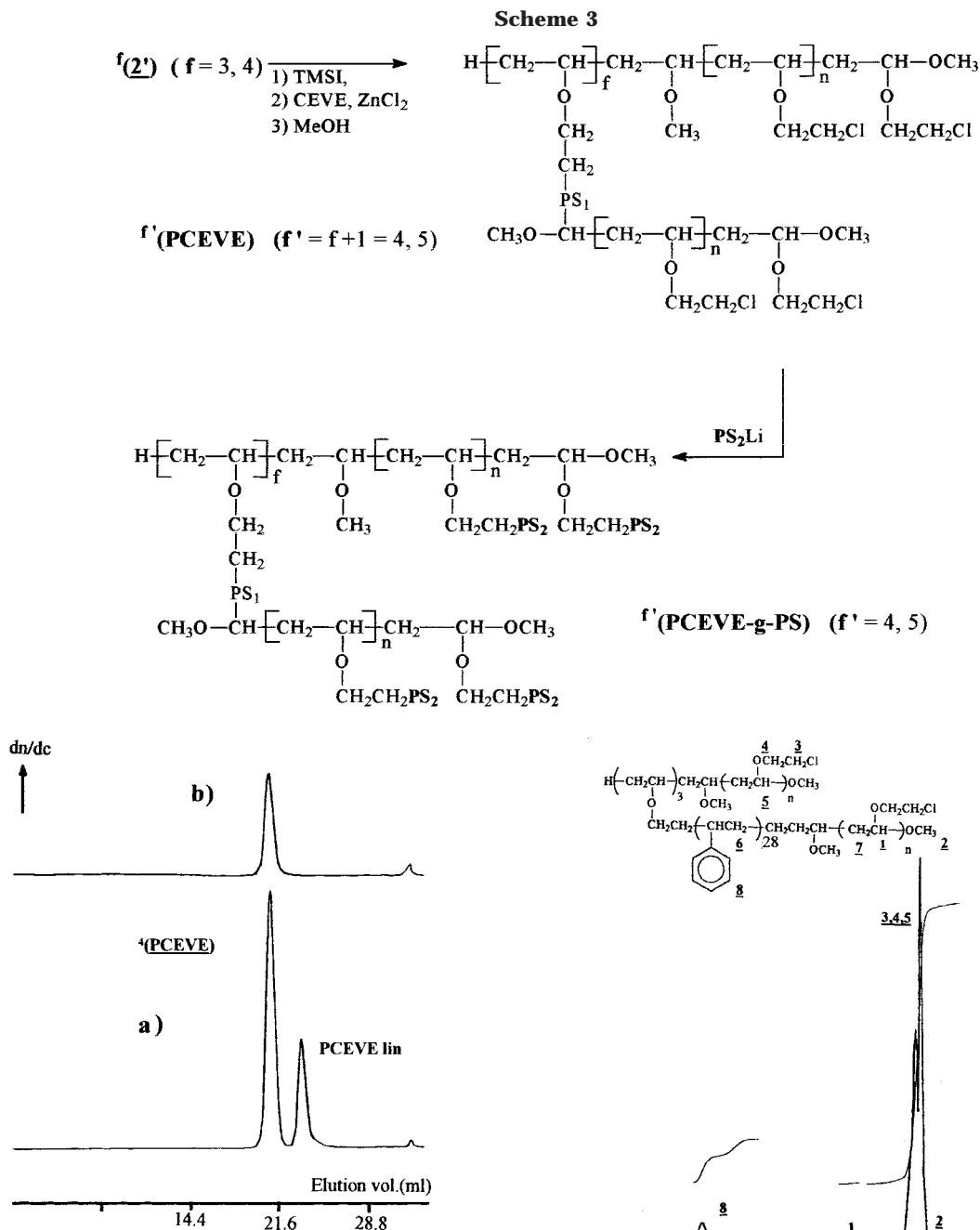
$$f = \frac{\bar{M}_{n \text{ app}}}{\bar{M}_{n \text{ PS branch}}} \left[ \frac{f^{1.5}}{[2 - f + 2^{0.5}(f - 1)]^3} \right]^{-1/\alpha + 1}$$

with the Mark–Houwink coefficient,  $\alpha = 0.71$ , also

**Table 1.** Star Poly(CEVE)- $g$ - $\omega$ -acetal polystyrene <sup>4</sup>(2') Prepared by Grafting  $\omega$ -Acetal PS<sub>1</sub>Li Oligomers onto Isometric PCEVE Oligomers (<sup>1</sup>)<sub>*n*</sub>

poly(CEVE) ( <sup>1</sup> ) <sub><i>n</i></sub> no. of CEVE units ( <i>n</i> )	poly(CEVE)- $g$ - $\omega$ -acetal polystyrene <sup>4</sup> (2') <sup>a</sup>							
	star PS ref <sup>a</sup>	10 <sup>-3</sup> $\bar{M}_n$ (th) <sup>b</sup> (g/mol)	10 <sup>-3</sup> $\bar{M}_n$ (SEC) (g/mol)		$\bar{M}_w/\bar{M}_n$	$\bar{M}_{n \text{ app}}(\text{RI})/\bar{M}_{n \text{ star}}(\text{LS})$	$g^{e,f}$	$f^{g,h}$
			LS <sup>c</sup>	RI <sup>d</sup>				
	$\omega$ -acetal PS <sub>1</sub> <sup>i</sup>			2.90	1.04			1
2	<sup>2</sup> (2')	6.07		6.00	1.02			3
3	<sup>3</sup> (2')	9.07	9.30	8.30	1.04	0.89	0.76 (0.78)	3.1 (3.2)
4	<sup>4</sup> (2')	12.05	12.20	10.40	1.04	0.85	0.69 (0.63)	3.6 (3.8)

<sup>a</sup> Exponent number indicates the number of branches for star polymers. <sup>b</sup> Calculated from the equation:  $n(2920 + 71) + 90$  with  $n$  = number of CEVE units. <sup>c</sup> Measured by light scattering in THF ( $dn/dc = 0.179$ , 25 °C). <sup>d</sup> Measured by refractive index detection on the basis of linear PS standards. <sup>e</sup> Calculated from the experimental relationship  $\bar{M}_{n \text{ app}}(\text{RI})/\bar{M}_{n \text{ star}}(\text{LS}) = g^{0.43}$ . <sup>f</sup> Values in parentheses correspond to  $g$  calculated from the expression  $g = (3f - 2)/f^2$  with  $f$  = number of branches equal to the number of CEVE units. <sup>g</sup> Number of branches  $f$  calculated from the relation  $g = (3f - 2)/f^2$  with  $g$  values determined according to footnote e. <sup>h</sup> Values of  $f$  in parentheses were obtained from the equation  $f = (\bar{M}_{n \text{ app}}/\bar{M}_{n \text{ PS branch}})[f^{1.5}/[2 - f + 2^{0.5}(f - 1)]]^{3/(\alpha + 1)}$  with  $\alpha$  the Mark–Houwink coefficient equal to 0.71. <sup>i</sup>  $\omega$ -Acetal PS graft.

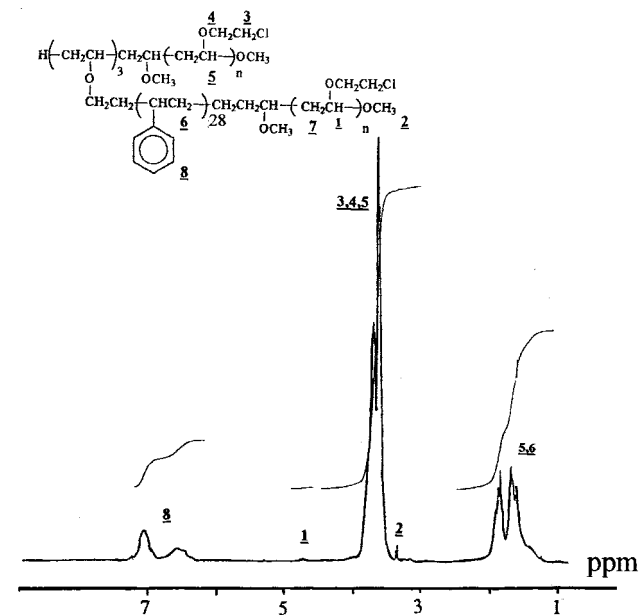


**Figure 3.** SEC chromatograms of the crude and purified four-branch star poly(CEVE),  $^4(PCEVE)$ , prepared from precursor  $^3(2')$ .

closely fits with the theoretical number of PS branches for the two samples.

Comb polymer  $^3(2')$ , with its four dimethoxy acetal functions at the end of the three PS branches and the one located at the backbone terminus, yields a tetrafunctional initiator for the CEVE polymerization by reaction with trimethylsilyl iodide.<sup>7</sup> Comb polymer  $^4(2')$ , which possesses five acetal groups and is potentially a pentafunctional precursor for the synthesis of five-arm star poly(CEVE), was prepared similarly.

**2. Synthesis of Four- and Five-Arm Poly(CEVE) Stars,  $^4(PCEVE)$  and  $^5(PCEVE)$ .** CEVE polymerizations using  $^3(2')$  and  $^4(2')$  as chain precursors, (Scheme 3), were performed under "living" conditions at  $-30^\circ\text{C}$  in toluene as previously described. Comb copolymers  $^3(2')$  and  $^4(2')$  were first derivatized into the corresponding  $\alpha$ -iodoether compounds by adding TMSI<sup>8</sup> (1.2 equiv



**Figure 4.**  $^1\text{H}$  NMR of the four-branch star poly(CEVE),  $^4(PCEVE)$ , prepared from precursor  $^3(2')$ .

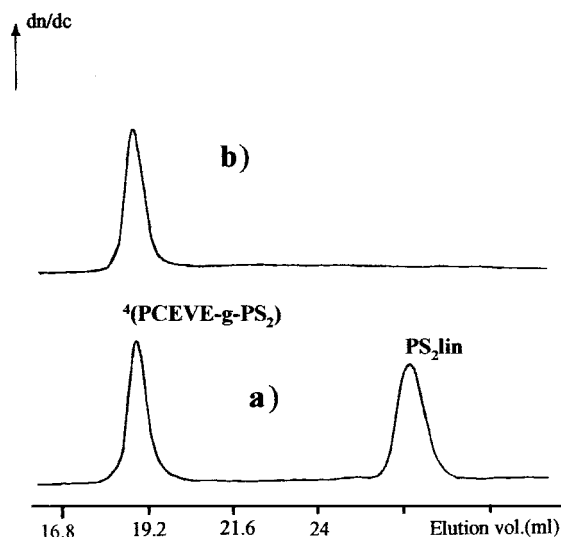
relative to acetal). Polymerizations were then started by introduction of  $\text{ZnCl}_2$  as catalyst. At the end of the polymerization the growing chains were deactivated by adding methanol/lutidine. The SEC chromatogram and the  $^1\text{H}$  NMR spectrum of the poly(CEVE) star polymers prepared from the tetrafunctional initiator  $^3(2')$  are presented in Figures 3 and 4, respectively. Although a small fraction of homopoly(CEVE) is generally formed by initiation by residual water (+TMSI), the main polymer fraction can be attributed to initiation by the multifunctional oligomer precursor. The star poly(CEVE) fraction was isolated by HPLC, and the total number of CEVE units per macromolecule was determined by  $^1\text{H}$  NMR from the relative integrals of CEVE units/styrene units of the precursor. Characteristics of



**Table 2. Poly(CEVE)-*g*-(polystyrene-*b*-poly(CEVE))<sup>*f*</sup>(PCEVE) Star Block Copolymers of *f*' Branches Prepared by CEVE Polymerization Initiated from the acetal termini of Poly(CEVE)-*g*- $\omega$ -acetal PS Oligomers<sup>*f*</sup>(2')**

star PS precursor <sup><i>a</i></sup> (2')		poly(CEVE)- <i>g</i> -(polystyrene- <i>b</i> -poly(CEVE)) <sup><i>f</i></sup> (PCEVE)								
		star PCEVE ref	10 <sup>-3</sup> $\bar{M}_n$ (SEC) (g/mol)		$\bar{M}_w/\bar{M}_n$	PCEVE branch $\overline{DP}_n$		$\bar{M}_n$ app(RI)/ $\bar{M}_n$ star(LS)	$g^{f,g}$	$f^{h,i}$
			LS <sup><i>b</i></sup>	RI <sup><i>c</i></sup>		NMR <sup><i>d</i></sup>	LS <sup><i>e</i></sup>			
3(2')	4	4(PCEVE)	53.8	46.3	1.04	107	105	0.86	0.68 (0.63)	3.7 (3.8)
4(2')	5	5(PCEVE)	57.4	42.7	1.04	95	86	0.75	0.52 (0.52)	5.0 (5.0)

<sup>*a*</sup> See Table 1. <sup>*b*</sup> Measured by light scattering in THF ( $dn/dc = 0.115$  for 4(PCEVE) and 0.110 for 5(PCEVE)). <sup>*c*</sup> Measured by refractive index detection relative to linear PCEVE. <sup>*d*</sup> Determined by NMR from the ratio CEVE units/ $f' \times$  styrene units, with  $f' =$  number of branches equal to the number of acetal groups/star PS chain precursor. <sup>*e*</sup> Calculated from the equation  $(\bar{M}_{n,LS}(PCEVE) - \bar{M}_{n,f'}(2')/106.5f')$  with  $f$  and  $f'$  number of branches indicated in the reference names. <sup>*f*</sup> Calculated from the equation<sup>3</sup>  $g^{0.43} = \bar{M}_{n,app}/\bar{M}_{n,star}$ . <sup>*g*</sup> Values in parentheses correspond to  $g$  determined from the empirical relation  $g = (3f' - 2/f'^2)$  with  $f'$  as in footnote *d*. <sup>*h*</sup> Number of branches calculated from the relation  $g = (3f' - 2/f'^2)$  with  $g$  values determined according to footnote *f*. <sup>*i*</sup>  $f'$  calculated from the equation,<sup>9</sup>  $f' = (\bar{M}_{n,app}/\bar{M}_{n,PS\ branch})[f'^{1.5}/[2 - f' + 2^{0.5}(f' - 1)]^3]^{-1/\alpha+1}$  with  $\alpha$  the Mark-Houwink coefficient equal to 0.71 determined in THF with PCEVE standards.

**Figure 5.** SEC chromatograms of the four-branch star comb, 4(PCEVE-*g*-PS<sub>2</sub>), prepared from star 4(PCEVE): (a) crude product; (b) product after purification by selective precipitation.

the *f*'(PCEVE) star polymers are given in Table 2. SEC data agree with the branched architecture of the poly(CEVE). The ratio  $\bar{M}_{n,app}/\bar{M}_{n,star}$  (i.e.,  $\bar{M}_{n,RI}/\bar{M}_{n,LS}$ ) yields a  $g$  value ( $g = (\bar{M}_{n,app}/\bar{M}_{n})^{0.43}$ ) which is consistent with a number of branches,  $f'$ , close to the number of acetal functions of the precursor.

**3. Poly(CEVE) Stars with Comblike PS Arms, 4(PCEVE-*g*-PS) and 5(PCEVE-*g*-PS).** Their preparation was achieved by grafting PSLi chains onto the poly(CEVE) stars 4(PCEVE) and 5(PCEVE) (Scheme 3).

The SEC chromatogram of the crude comblike star copolymer obtained from 5(PCEVE), and PS<sub>2</sub> graft of  $\overline{DP}_n = 26$  is presented in Figure 5. The signal at lower elution volume corresponds to the poly(CEVE)-*g*-polystyrene star copolymer 5(PCEVE-*g*-PS). The peak is unimodal and quite narrow ( $\bar{M}_w/\bar{M}_n < 1.2$ ), which is consistent with a clean grafting process. The second polymer population corresponds to deactivated PS<sub>2</sub>Li. Because of the large difference in their molar masses the star polymer fraction, was easily separated from ungrafted polystyrene by selective precipitation in a mixture of cyclohexane/*n*-heptane.

The characteristics of the poly(CEVE) stars with comblike polystyrene arms, 4(PCEVE-*g*-PS) and 5(PCEVE-*g*-PS), are collected in Table 3. The theoretical molar masses of the graft copolymers, calculated from the  $\overline{DP}_n$  of the star poly(CEVE) backbone and the  $\bar{M}_n$  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. In contrast the apparent molar masses using RI detection are much lower as expected for hyperbranched polymer structures. The number of PS<sub>2</sub> grafts per poly(CEVE) branch,  $F$ , was estimated from the ratio  $(\bar{M}_{n,LS\ graft\ copolymer} - \bar{M}_{n,precursor})/f' \times \bar{M}_n(PS_2)$ . The results closely fit with the number of monomer units in the star poly(CEVE) backbone, in agreement with almost complete substitution of the chloroethyl ether groups.

**4. Dimensions and Solution Properties of 4(PCEVE-*g*-PS) and 5(PCEVE-*g*-PS).** The impact of the comb chain topology on the dimensional parameters and solution behavior was investigated in THF at 25 °C. To better determine the effect of the backbone architecture, a series of "linear" PS combs ( $\overline{DP}_n$  of

**Table 3. Synthesis and Characterization of poly(CEVE)-*g*-(polystyrene-*b*-(poly(CEVE)-*g*-polystyrene)), *f*'(PCEVE-*g*-PS) Comb Star Polymers with *f* Branches, Obtained by Grafting PS<sub>2</sub>Li onto Poly(CEVE)-*g*-(polystyrene-*b*-poly(CEVE)), *f*'(PCEVE) Star Copolymers**

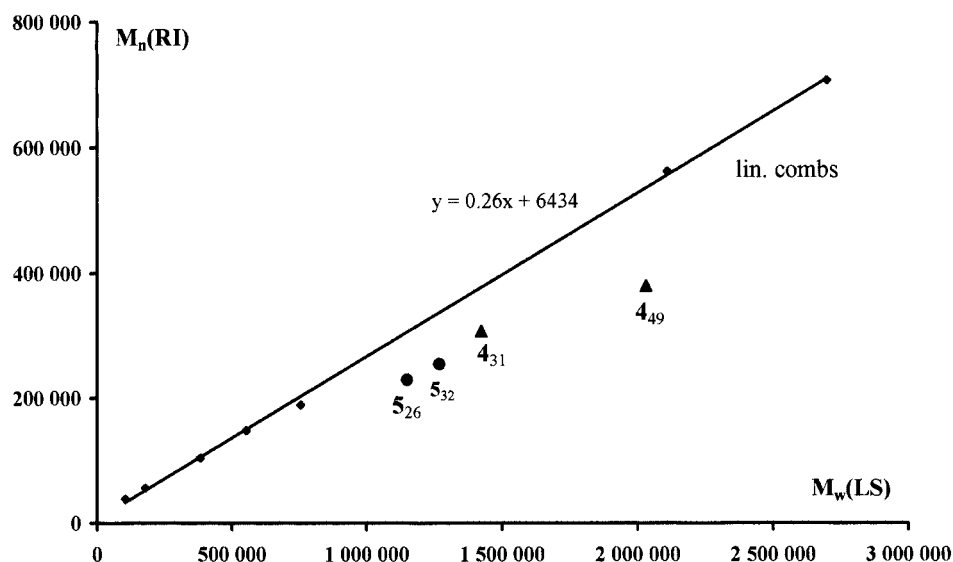
backbone star polymer <sup><i>a</i></sup> (PCEVE)		poly(CEVE)- <i>g</i> -(polystyrene- <i>b</i> -(poly(CEVE)- <i>g</i> -polystyrene)) <i>f</i> '(PCEVE- <i>g</i> -PS)											
		PS <sub>2</sub> graft $\overline{DP}_n$ <sup><i>b</i></sup>	ref	10 <sup>-6</sup> $\bar{M}_n$ (th) (g/mol)		10 <sup>-6</sup> $\bar{M}_n$ (SEC) (g/mol)		$\bar{M}_w/\bar{M}_n$	$F^{f,d}$	$[\eta]^e$ (dL/g)	$R_{\eta}^f$ (nm)	$R_g$ (nm)	$R_h$ (nm)
				branch $\overline{DP}_n$	LS <sup><i>c</i></sup>	RI <sup><i>b</i></sup>	LS <sup><i>c</i></sup>						
4(PCEVE)	105	48	4(PCEVE- <i>g</i> -PS)	2.15	0.38	2.03	1.09	102	0.20	18	18.5	18	1.02
4(PCEVE)	105	30	4(PCEVE- <i>g</i> -PS)	1.36	0.31	1.42	1.06	110	0.18	16	16	16	1.00
5(PCEVE)	86	26	5(PCEVE- <i>g</i> -PS)	1.22	0.22	1.15	1.07	82	0.18	14.8	13.2	14	0.94
5(PCEVE)	86	31	5(PCEVE- <i>g</i> -PS)	1.44	0.25	1.27	1.07	75	0.18	15.4	14.3	16	0.89

<sup>*a*</sup> See Table 2. <sup>*b*</sup> Determined by SEC relative to linear PS. <sup>*c*</sup> Determined by SEC in THF using light scattering detection ( $dn/dc = 0.179$ , 633 nm, 25 °C). <sup>*d*</sup> Number of PS grafts per PCEVE branch calculated using the expression  $(\bar{M}_{n,LS} - \bar{M}_{n,f'}(PCEVE)/f' \bar{M}_n(PS))$ . <sup>*e*</sup> Determined by SEC in THF at 25 °C. <sup>*f*</sup> Calculated from the Einstein equation  $[\eta] = (10\pi/3)N_A(R_{\eta}^3/M)$ . <sup>*g*</sup>  $\rho = R_g/R_h$ .

**Table 4. Solution Characteristics of a Series of Linear Poly(CEVE)-*g*-polystyrene Comb Polymers of Increasing Backbone Length and Identical PS Grafts<sup>3</sup>**

(PCEVE- <i>g</i> -PS) linear combs								
ref	10 <sup>-5</sup> $\bar{M}_n$ (g/mol)		$\bar{M}_w/\bar{M}_n$	$[\eta]^c$ (dL/g)	$R_\eta^d$ (nm)	$R_g$ (nm)	$R_h$ (nm)	$\rho = R_g/R_h$
$\overline{DP}_n^{\text{PCEVE}} - \overline{DP}_n^{\text{PS}}$	RI <sup>a</sup>	LS <sup>b</sup>						
60–30	0.57	1.79	1.03	0.09	6.3		6.2	
134–30	1.05	3.83	1.02	0.11	8.7	12	7.9	1.52
214–30	1.49	5.54	1.02	0.14	10.7	14.5	10.1	1.43
282–30	2.72	7.55	1.03	0.17	12.7	20	11.8	1.69
764–30	5.63	21.10	1.03	0.40	23.7	33	19.2	1.72
1042–30	7.08	27.00	1.03	0.47	27.2	39.8	21.5	1.85

<sup>a</sup> Determined by SEC relative to linear PS. <sup>b</sup> Determined by SEC in THF using a light scattering detection ( $dn/dc = 0.179$  at 25 °C). <sup>c</sup> Measured in THF, at 25 °C. <sup>d</sup> Calculated from the Einstein equation  $[\eta] = (10\pi/3)N_A(R_{\eta}^3/M)$ .

**Figure 6.** Evolution of apparent molar masses of linear combs and star combs, determined by SEC on the basis of linear PS standards, vs absolute molar masses measured by light scattering.**Table 5. Relation between Linear Combs (PCEVE-*g*-PS), L-C, and Star Combs <sup>f</sup>(PCEVE-*g*-PS), S-C, Polymers with both the Same PCEVE Backbones  $\overline{DP}_n$  and the Same PS Grafts  $\overline{DP}_n$** 

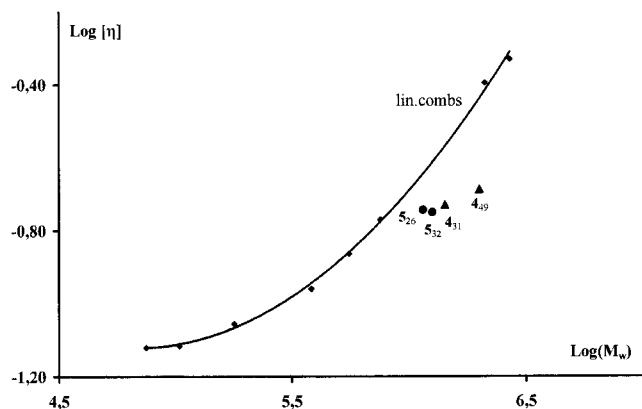
ref of star comb <sup>f</sup> (PCEVE- <i>g</i> -PS)	$\overline{DP}_n$ <sup>a</sup>		poly(CEVE)- <i>g</i> -(polystyrene- <i>b</i> -(poly(CEVE)- <i>g</i> -polystyrene)), comb star						
	PCEVE branch	PS graft	S-C 10 <sup>-5</sup> app $\bar{M}_n$ <sup>a</sup> (g/mol)	L-C 10 <sup>-5</sup> eq app $\bar{M}_n$ <sup>b</sup> (g/mol)	$\bar{M}_n$ eq L-C $\bar{M}_n$ eq L-C	$R_{g \text{ eq L-C}}$ (nm) <sup>c</sup>	$R_{g \text{ S-C}}^2$ d/ $R_{g \text{ eq L-C}}^2$	$g_{th}^e$	$[\eta]$ eq lin comb <sup>f</sup>
<sup>4</sup> (PCEVE- <i>g</i> -PS)	105	30	3.10	3.77	0.81	26.8	0.36	0.62	0.27
<sup>5</sup> (PCEVE- <i>g</i> -PS)	86	31	2.50	3.37	0.75	25.8	0.36	0.52	0.24
<sup>5</sup> (PCEVE- <i>g</i> -PS)	86	26	2.29	3.06	0.75	23.6	0.40	0.52	0.22

<sup>a</sup> Determined by SEC relative to linear PS. <sup>b</sup> Calculated from  $M_n \text{ eq lin} = M_n \text{ LS} \times 0.26 + 6434$  (see Figure 6). <sup>c</sup> Calculated from  $\log(R_{g \text{ eq L-C}}) = \log(M_w \text{ S-C} \times 0.6 - 2.28)$  (see Figure 8). <sup>d</sup> See Table 3. <sup>e</sup> Calculated from  $g = 3f - 2/f^2$  with  $f$  = number of branches. <sup>f</sup> Calculated from Figure 7.

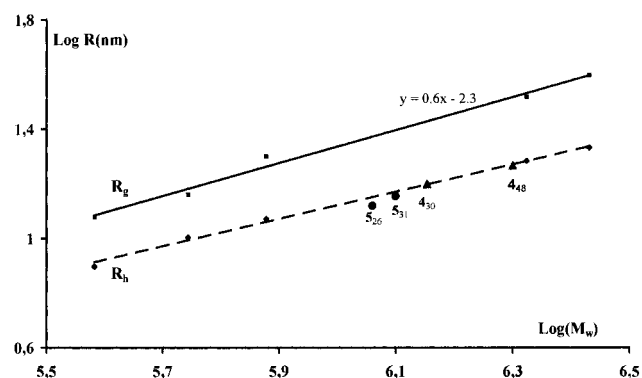
PS branches = 30) was synthesized and their solution characteristics determined. Data are collected in Table 4.

Figure 6 plots the apparent molar masses of linear and star comb polymers, determined by SEC relative to linear PS standards, vs absolute molar masses measured by light scattering. As expected, the star combs exhibit a lower apparent molar mass than the corresponding linear combs, due to their smaller hydrodynamic volume. Indeed, the ratio of the apparent molar mass of four and five branch comb stars and linear combs of equivalent  $\bar{M}_w$ , (Table 5) are close to those observed between stars and linear polymers (Table 2). The contraction factor  $g$  ( $R_{g \text{ star comb}}^2/R_{g \text{ lin. comb}}^2$ ) is however much smaller (larger contraction) than calculated using the empirical relationship,  $g_{th} = 3f - 2/f^2$ , developed for linear and star polymers with  $f$  branches.

The values of the intrinsic viscosity  $[\eta]$ , and of the different characteristic radii,  $R_g$ ,  $R_h$ , and  $R_{\eta}$  can be compared with the comb stars of relatively similar backbone  $\overline{DP}_n$  and PS branch length in Table 3. An easier comparison can be made from Figures 7 and 8. The logarithmic variations of  $[\eta]$  and of the gyration radius  $R_g$  and hydrodynamic radius  $R_h$  are plotted vs the molar mass both for a series of "linear" PS combs and for the corresponding comb stars <sup>4</sup>(PCEVE-*g*-PS) and <sup>5</sup>(PCEVE-*g*-PS) of almost identical PS branches (i.e.,  $\overline{DP}_n = 30-32$ ). For comb macromolecules of the same molar mass,  $[\eta]$  and  $R_g$  decrease when going from linear to the star backbone architecture. This is consistent with a more compact structure in the highly branched starlike macromolecules.<sup>10,11</sup> The  $R_h$  values, however, remains very close for the linear comb and star comb series. This similarity may be interpreted by a same



**Figure 7.** Logarithmic variations of  $[\eta]$  (THF, 25 °C) vs the molar mass for a series of "linear" PS combs with PS branches of  $\overline{DP}_n = 30$  (full line) and for the corresponding comb stars  $^4(\text{PCEVE-}g\text{-PS}_2)$  (▲) and  $^5(\text{PCEVE-}g\text{-PS}_2)$  (●). The subscript number gives the  $\overline{DP}_n$  of the PS branches.



**Figure 8.** Logarithmic variations of  $R_g$  and  $R_h$  vs the molar mass for a series of "linear" PS combs with PS branches of  $\overline{DP}_n = 30$  (full line and dashed line) and for the corresponding comb stars  $^4(\text{PCEVE-}g\text{-PS}_2)$  (▲) and  $^5(\text{PCEVE-}g\text{-PS}_2)$  (●). The subscript number gives the  $\overline{DP}_n$  of the PS branches. For the comb stars, the  $R_g$  and  $R_h$  values are almost identical.

resistance to penetration of solvent molecules into the clouds of connected branches whatever the backbone architecture.

Indeed, although determined under good solvent conditions (THF)  $R_g$ ,  $R_h$ , and  $R_\eta$  of PS comb stars are very close (Table 3), contrary to what is observed for linear combs (Table 4). For the four branch PS comb, the  $\rho$  factor ( $\rho = R_g/R_h$ ) is equal to one and decreases to near 0.9 for the five-arm comb macromolecules. This

places these macromolecular objects in the range of stars with a large number of arms<sup>12,13</sup> and dendrimers<sup>14</sup> ( $\rho = 0.977$ ) close to theoretical homogeneous hard sphere (theor.  $\rho = 0.778$ <sup>15</sup>). In similar conditions, the linear combs (Table 4) exhibit a much higher  $\rho$  value. Moreover, its value tends to increase with the linear backbone length. This may be attributed to the changes in the shape and behavior of linear comb macromolecules from star to wormlike.<sup>3,16,17</sup> Therefore, in highly branched macromolecules the shape factor is as important as the degree of branching in determining the  $R_g/R_h$  values.

Further investigation of the behavior and characteristics in solution and in the bulk of these highly branched star molecules, as well as the synthesis of new macromolecular objects based on covalent molecular assembling of elementary building blocks macromolecules are in progress.

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