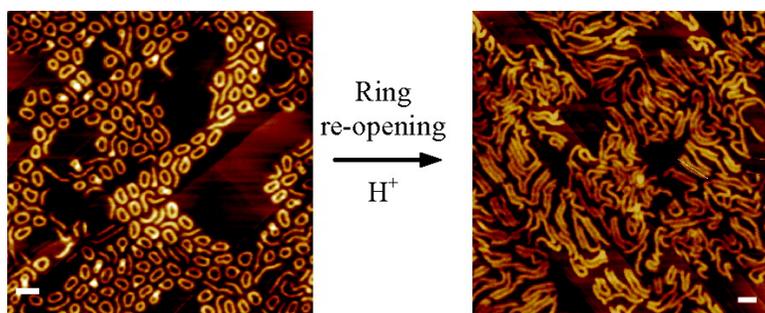


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AFM imaging of cyclic and linear Combs

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## Atomic Force Microscopy Imaging and Dilute Solution Properties of Cyclic and Linear Polystyrene Combs

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**Abstract:** Large macrocyclic poly(chloroethyl vinyl ether)s (PCEVE)s of controlled ring size and narrow distribution were synthesized by a ring-closure process involving the intramolecular formation of acetal linkages between the two external blocks of linear ABC triblock precursors prepared by living cationic polymerization. The corresponding shape-persistent ring P(CEVE-*g*-PS) combs having macrocyclic poly(chloroethyl vinyl ether) backbones and polystyrene side chains were then synthesized by a “grafting onto” technique and characterized by size exclusion chromatography (SEC) analysis and atomic force microscopy (AFM) imaging of isolated molecules. Quantitative hydrolysis of the acetal linkages of the macrocyclic PCEVE backbone in acidic conditions yields the linear poly(chloroethyl vinyl ether)-*g*-polystyrene homologue and allows a direct comparison of the characteristics and dimensions of cyclic and linear comb architecture. The influence of the chain architecture and PS graft dimensions on the dilute tetrahydrofuran (THF) solution properties, radius of gyration, and hydrodynamic radius of the comb copolymers is also studied and compared to data reported for linear and cyclic polystyrene chains.

### Introduction

Shape-persistent molecules have attracted a large interest over the past years as potential materials for nanotechnologies. Among this class of molecular objects, polymers occupy an important place. Examples include dendrimers,<sup>1–11</sup> hyperbranched polymers,<sup>12–15</sup> polymacromonomers<sup>16,17</sup> or other comblike polymers and copolymers,<sup>18–22</sup> with linear or more complex architecture. In such polymers, the shape persistency mainly results from the compactness of the macromolecules<sup>23–25</sup> thanks to their high branching density.

Another class of polymers with very unique chain architecture is the one constituted by macromolecular rings.<sup>26</sup> The synthesis

of macrocycles has been a challenging domain for polymer chemists for many years, and numerous synthesis strategies have been explored.<sup>26–36</sup> Although these endless chains have quite specific properties, because of their still flexible chain they do not exhibit the characteristics of shape-persistent objects. To improve chain stiffness the use of macrocycles bearing grafted chains has also been explored,<sup>37–41</sup> but since ring sizes remained low as compared to the grafts no evidence for a ring shape organization could be found. Indeed, although some fascinating properties can be expected for these ring shape-persistent

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macromolecules, both as isolated object and as self-assembled systems,<sup>42,43</sup> up to now very few studies have been focused on their synthesis.

Recently we have reported a new route to prepare very large polymer macrocycles of controlled molar mass and narrow polydispersity based on the intramolecular coupling of external blocks of an ABC linear precursor, as well as their derivatization into the corresponding ring polystyrene combs.<sup>44</sup> In this paper we extend this approach to the design of a series of shape-persistent macrocyclic polystyrene combs with different dimensions as well as the selective reopening of this rings in order to obtain the corresponding linear structures. The characteristics of the cyclic and linear combs are finally investigated in the solid by means of atomic force microscopy (AFM) imaging and in solution using size exclusion chromatography (SEC) and light scattering techniques.

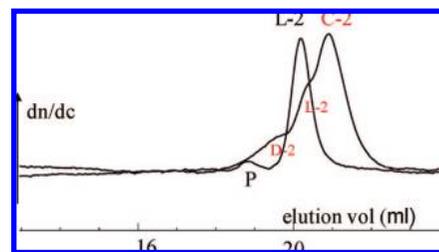
## Experimental Section

**Materials.** Commercial chloroethyl vinyl ether (CEVE, Acros Organics 99.5%), and 1,4-cyclohexanedimethanol divinyl ether (Sigma-Aldrich, 99%) were distilled twice over CaH<sub>2</sub> before use. Tetrahydrofuran (THF) was distilled over CaH<sub>2</sub>, stored over sodium benzophenone, and cryodistilled just before use. Toluene (99.5%, J.T. Baker, Deventer, The Netherlands) was purified by distillation over calcium hydride and stored over polystyryllithium seeds. *tert*-Butyldimethylsilyloxy vinyl ether (SiVE) was prepared as described previously by Fukui et al.<sup>45</sup> from 2-hydroxyethyl vinyl ether (supplied by Maruzen Petrochemical) and distilled over calcium hydride twice before use. Pyridinium *p*-toluenesulfonate (PTSA, supplied by Sigma-Aldrich) and ZnCl<sub>2</sub> (Aldrich) were used without purification. The anhydrous hydrogen iodide/toluene solution was obtained as previously described.<sup>46</sup> Tetrabutylammonium fluoride/THF solution (Bu<sub>4</sub>NF, 1 M, Aldrich) was used as received. Polystyrenyldiphenylhexyllithium (PSDPELi) was prepared as described previously.<sup>46</sup>

**Techniques.** <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 MHz in CDCl<sub>3</sub>.

Right Angle Laser Light Scattering (RALLS) measurements, molecular weights and radius of gyration  $R_g$ , were measured on a Waters apparatus equipped with refractive index 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). THF was used as a carrier solvent at a flow rate of 1.0 mL/min. Calibration in the case of refractive index detection was performed using linear polystyrene or linear poly(chloroethyl vinyl ether) (PCEVE).

Samples for AFM analysis were prepared by solvent casting at ambient conditions by spin coating on substrates starting from



**Figure 1.** SEC of a linear ABC poly(HEVE-*b*-CEVE-*b*-CDVE) **4** linear triblock copolymer (sample L-2, Table 1) and of the corresponding copolymer after cyclization (C-2). P is the fraction of linears which are formed through CDVE coupling. L-2 and D-2 are remaining linears and polycondensates (mainly dimers).

solutions in dichloromethane. Practically, one drop of a dilute solution (0.01 wt %) was spin cast on a 1 × 1 cm<sup>2</sup> freshly cleaved highly oriented pyrolytic graphite (HOPG). All AFM images were recorded in air with a 3100 Dimension microscope (Digital Instruments, Santa Barbara, CA), operated in tapping mode. The probes were commercially available silicon tips with a spring constant of 40 N/m, a resonance frequency lying in the 270–320 kHz range, and a radius of curvature of 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.

Dynamic light scattering measurements (hydrodynamic radius  $R_h$ ) 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.

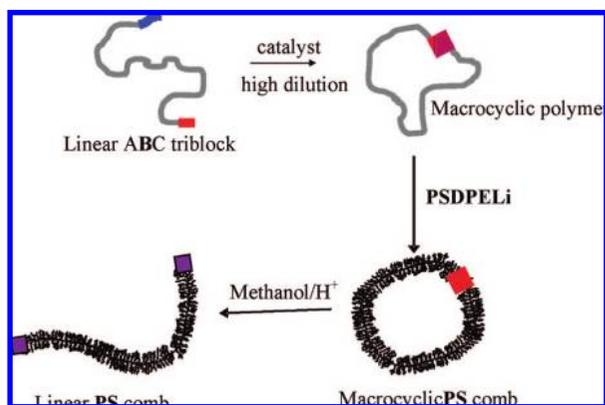
**Polymer Synthesis.** Polymerization was carried out under vacuum. The sequential polymerization procedure was as follows: 20 mg (0.19 mmol) of CEVE and (0.1 mmol) of HI/toluene was added to 80 mL of dry toluene under vacuum at –12 °C to form the initiator. After 10 min, an initial amount of SiVE (0.4 g, 2.02 mmol) was introduced in the solution and the polymerization was triggered by the addition of 23 mg of ZnCl<sub>2</sub> (0.17 mmol) dissolved in 2 mL of ether. After 1 h, the second monomer CEVE (15 g, 0.141 mol) was added, and the polymerization was continued until the desired molar mass of the diblock P(SiVE-*b*-CEVE) **2** was reached. Then cyclohexanedimethanol divinyl ether (CDVE) (7 g, 35 mmol) was added in the reaction mixture, and after 15 min the polymerization was terminated with prechilled methanol containing a small amount of aqueous ammonia solution. The reaction mixture was slowly precipitated twice into methanol yielding 11 g of block copolymer. The weight average molecular weight ( $\bar{M}_w = 83.8 \times 10^3$ ) was determined by SEC coupled with multiangled laser light scattering in THF. Exact composition of the triblock PSiVE-*b*-PCEVE-*b*-PDVE **3** was determined by <sup>1</sup>H NMR; see Figure S1a in the Supporting Information.

Deprotection of silyl group was as follows: 1 g of the triblock PSiVE-*b*-PCEVE-*b*-PDVE ( $1.8 \times 10^{-5}$  equiv of silyl ether groups) was dissolved in dry THF and dried by solvent evaporation. Then polymer **3** was dissolved again in 30 mL of dry THF and Bu<sub>4</sub>NF in THF (2 mL, 2.0 mmol) under nitrogen. After 15 min the solution was concentrated and the polymer was precipitated in MeOH, yielding 1.8 g of POHVE-*b*-PCEVE-*b*-PDVE triblock copolymer **4**. Complete deprotection of the silyl groups was confirmed by <sup>1</sup>H NMR; see Supporting Information Figure S1b.

**Cyclization Procedure.** After drying three times the triblock copolymer **4** by solubilization in dry THF (3 × 30 mL) and solvent evaporation, the copolymer ( $\bar{M}_n = 83.8 \times 10^3$  g/mol,  $\bar{M}_w/\bar{M}_n = 1.05$ , 71.4 mg,  $6.66 \times 10^{-7}$  mol) was dissolved in 300 mL of dry toluene. Then a solution of pyridinium *p*-toluene sulfonic acid salt (PTSA) (17 mg,  $2 \times 10^{-5}$  mol) in dry THF (2 mL) was added, and the reaction mixture was stirred at 20 °C for a few hours. The cyclization was followed by SEC, and after maximal transformation of the linear precursor into the acetal-linked macrocycle the polymer was submitted to the grafting step without further purification.

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Scheme 1



**PS Grafting Procedure.** A solution of polystyrenyldiphenylhexyl lithium (10 g PSDPELi,  $\bar{M}_n = 10\,000$  g/mol,  $\bar{M}_w/\bar{M}_n = 1.03$ ) in cyclohexane (100 mL) was placed in a burette and incrementally added to the cyclic PCEVE (60 mg). PSLi was added until the fading pink color of the reacting media remained over a 3 day period. Residual PSLi was finally deactivated by adding degassed methanol. Due to the important difference in their molar masses, separation between the comb copolymer on the one hand and the linear unreacted PS on the other hand was readily achieved by selective precipitation of the combs into a cyclohexane/heptane mixture. Yield: 5.4 g,  $\bar{M}_w$  LS =  $7.6 \times 10^6$  g/mol.

**Purification of the Cyclic Polystyrene Comb.** The fraction of linears (unimer and dimers) and of cyclic dimers could be significantly reduced by their preferential precipitation from a cyclohexane solution upon gradually and slowly decreasing the temperature from 20 to 18 °C. Typically 1 g of cyclic brushes was

dissolved in 100 mL of cyclohexane at 25 °C. The solution was maintained at constant temperature in a thermostatic bath for 1 to 2 h, and then the temperature was decreased slowly and incrementally to allow selective precipitation of linears and of various dimers. Evolution of the composition of the soluble fraction was followed by SEC analysis. Yield in recovered cyclic-rich fraction was in the range of 500–600 mg.

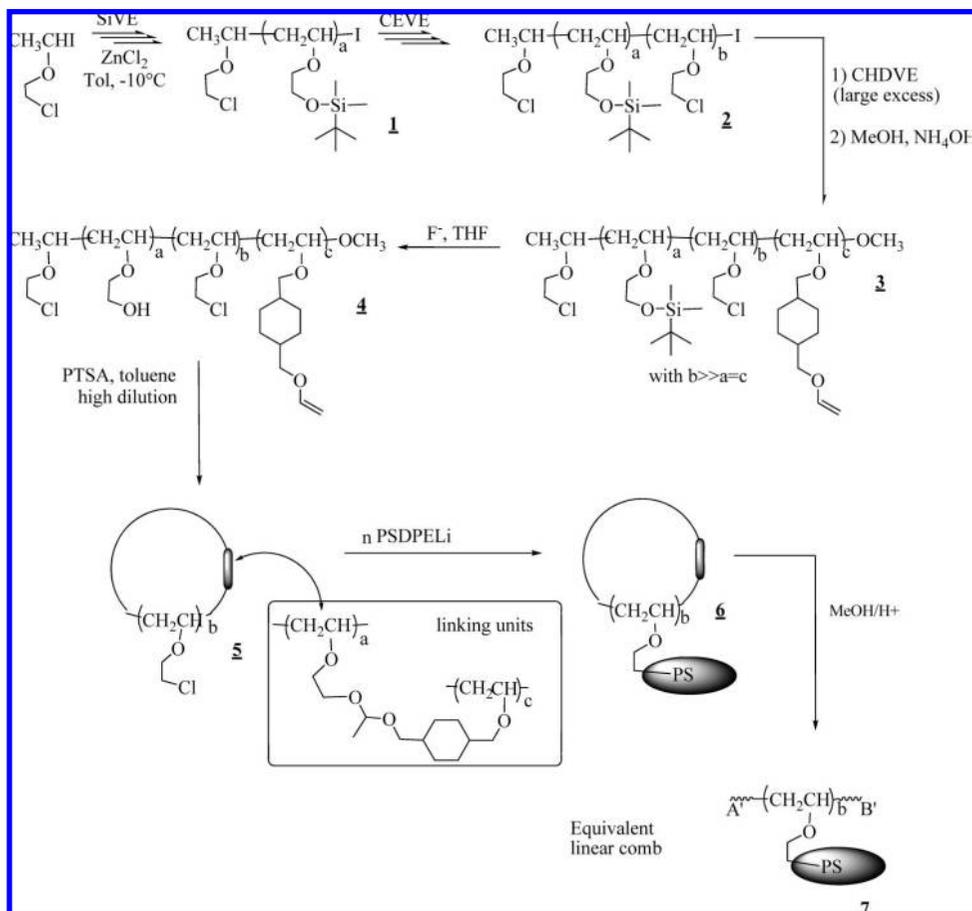
For the static and quasi-elastic light scattering measurements, the cyclic PS combs were purified by SEC chromatography fractionation of small amounts of crude samples (8 mg). The fractionated samples contained about 80% of cyclic PS combs.

**Ring Reopening: Preparation of Linear Homologues.** In a THF solution of cyclic PS brushes (20 mg/mL), was added 1% in volume of an acidic methanol solution (MeOH/HCl, 75/25 v/v), and the solution was stirred at 20 °C until complete disappearance of the peak of cyclic combs on the SEC chromatogram. The polymer was then recovered by precipitation into methanol and further characterized by AFM and various techniques.

## Results and Discussion

The new approach recently developed in our laboratory<sup>44</sup> for the preparation of large ring polymers, Scheme 1, is based on the preparation of linear ABC triblock copolymers, in which the long central B block is surrounded by two short A and C sequences constituted of monomer units bearing reactive antagonist functions. In a second step these triblocks are reacted in presence of a catalyst under highly dilute conditions to form a macrocycle by intramolecular coupling of the A and C block functions. The synthetic route is detailed in Scheme 2. The ABC triblocks **3** were synthesized by sequential living cationic copolymerization successively of SiVE, CEVE as monomer for the central block, and CDVE. To avoid or strongly limit reaction

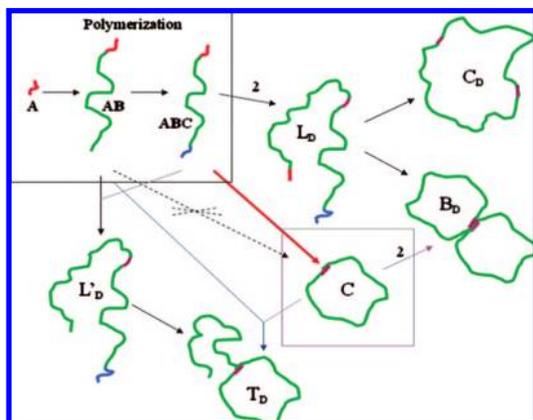
Scheme 2



**Table 1.** Characteristics of Linear (L) ABC Triblocks Prepared by Living Cationic Polymerization and of the Corresponding Cyclic (C) with Poly(CEVE) as Central Block

triblock ABC	$M_n \times 10^{-3}^a$	$M_p \times 10^{-3}^a$	$M_w/M_n$	$M_{pD}/M_{pL}$	$M_w \times 10^{-3}^b$	$DP_n A$ (SiVE) <sup>c</sup>	$DP_n B$ (CEVE) <sup>d</sup>	$DP_n C$ (CDVE) <sup>e</sup>	estimated cyclization yield % <sup>f</sup>
L-1	64.24	71.25	1.05	0.80	59.2	3	548	2	70
C-1	52.68	71.25	1.21						
L-2	83.80	95.42	1.05	0.79	83.8	5	774	4	65
C-2	67.04	67.04	1.17						
L-3	103.98	117.50	1.06	0.78	104.7	12	956	3	68
C-3	81.10	91.50	1.15						

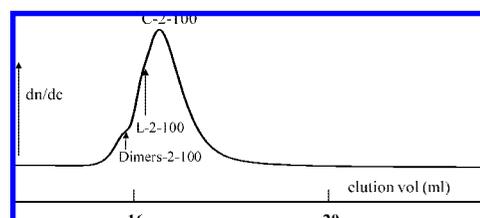
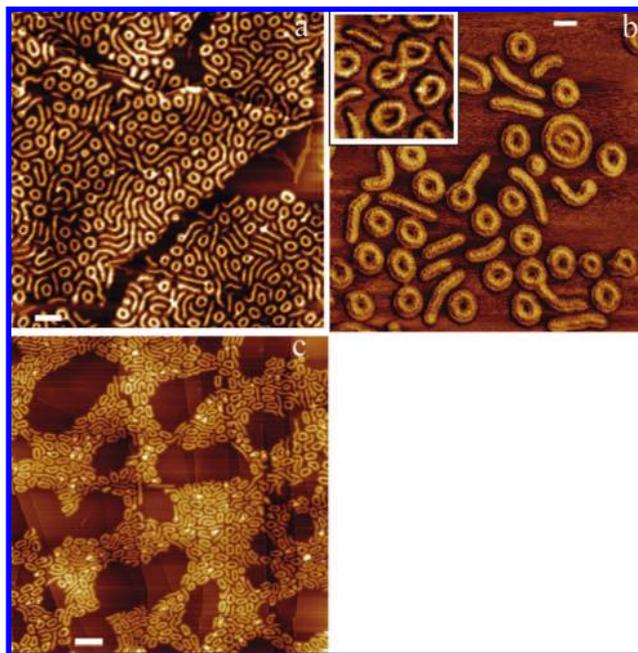
<sup>a</sup> Determined by SEC in THF by means of PS standards. <sup>b</sup> Measured by SLS with a refractive index increment ( $dn/dc$ ) of 0.09. <sup>c</sup> Determined by <sup>1</sup>H NMR from integration ratio between CEVE protons (calculated from  $M_w/P_{CEVE}$ ) and  $(CH_3)_2Si$  protons. <sup>d</sup> Calculated from  $(M_w/sls - (M_n/SiVE + M_n/CDVE))$ . <sup>e</sup> Calculated by <sup>1</sup>H NMR from the relative integration of CDVE vinyl ether protons. <sup>f</sup> From deconvolution of SEC peaks.

**Scheme 3.** Possible Pathways for the Formation of the Various Linear and Cyclic Chain Architectures

of the second vinyl ether function of CDVE, which may yield interchain coupling, its polymerization was stopped at very low conversion (<10%). The characteristics of the linear triblocks were determined by SEC, see Figure 1, and by <sup>1</sup>H NMR, see Figure S1a in the Supporting Information. Results are collected in Table 1. For the linear triblock L-1, degree of polymerization ( $\overline{DP}_n$ ) values are 548, 3, and 2, for the central PCEVE B block and the A and C sequences, respectively. For the larger linears L-2 and L-3 the PCEVE  $\overline{DP}_n$ 's are 774 and 956, respectively, whereas the external blocks remain limited to a very small number of monomer units, in the range of 3–12.

Deprotection of the hydroxyl groups of the SiVE sequence was readily achieved by reaction of the triblock copolymer with tetrabutylammonium fluoride (TBAF) in THF, thus yielding hydroxyethyl vinyl ether (HEVE) units and the corresponding poly(HEVE-*b*-CEVE-*b*-CDVE) linear triblock **4**, with unchanged total  $\overline{DP}_n$  and molar mass distribution. The quantitative removal of the *tert*-butyldimethylsilyl group was confirmed by the absence of the corresponding proton signals on the <sup>1</sup>H NMR spectrum; see Figure S1b in the Supporting Information.

**Cyclization.** The intramolecular coupling between the hydroxyl functions of the HOVE units of block A and the pendant vinyl ether functions of block C was achieved in dry toluene under high dilution, in the presence of PTSA as catalyst. The reaction between hydroxyl functions and vinyl ether groups yield the rapid formation of acetal links between the A and C sequences, as described in Scheme 2. The SEC chromatogram of the crude polymer **5** after the cyclization step is shown Figure 1. A strong shift of the main SEC peak toward higher elution volume is observed indicating a decrease in the hydrodynamic volume of the macromolecule, in agreement with chain cyclization. For all samples, the ratio between the apparent molar mass ( $M_{peak}$ ) of the cyclic and of the linear ABC copolymers is close

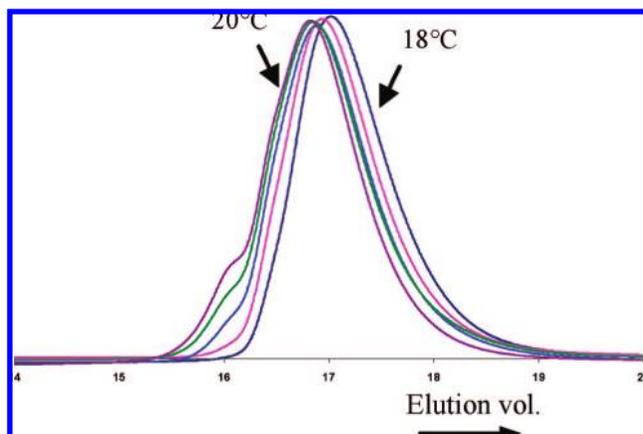
**Figure 2.** SEC chromatogram of a cyclic PS comb obtained after elimination of excess of ungrafted PS (sample C-2-100, Table 2).**Figure 3.** AFM images of crude and fractionated polystyrene cyclic combs (sample C-2-100, Table 2) obtained from deposits of their THF solution on HOPG; only the fraction of ungrafted PS has been eliminated; (a) general view of the crude sample (height image scale bar, 200 nm); (b) magnified phase image (scale bar, 100 nm) showing some of the other comb architectures formed (see Scheme 3); (c) enriched cyclic fraction obtained by temperature-induced selective precipitation (height image, scale bar, 200 nm).

to 0.8; see data in Table 1. Considering that the size reduction due coupling of A and C sequences is negligible with respect to the B block length, these results are fully consistent with previously reported data for cyclized polymers.<sup>31,32,40</sup> However, as it may be noticed on the SEC chromatogram, Figure 1, a significant peak broadening of the cyclized polymer is observed. In the high molar mass range two peak shoulders indicate the presence both of remaining linear ABC precursor and of other linear or cyclic structures of higher molar masses, likely issued

**Table 2.** Dimensions of Cyclic PS Combs as Determined by Measurements on AFM Images

PS comb reference	$\overline{DP}_n$ PCEVE (B block)	circumference (nm)		
		calcd <sup>a</sup>	measd <sup>b</sup>	ring diameter (nm)
C-1-100	548	137	122	94
C-1-170	548	137	116	96
C-2-100	774	193	188	105
C-3-170	956	239	250	127

<sup>a</sup> Calculated on the basis of a complete chain extension (C–C bond = 0.25 nm). <sup>b</sup> Measured at the center of the ring section.

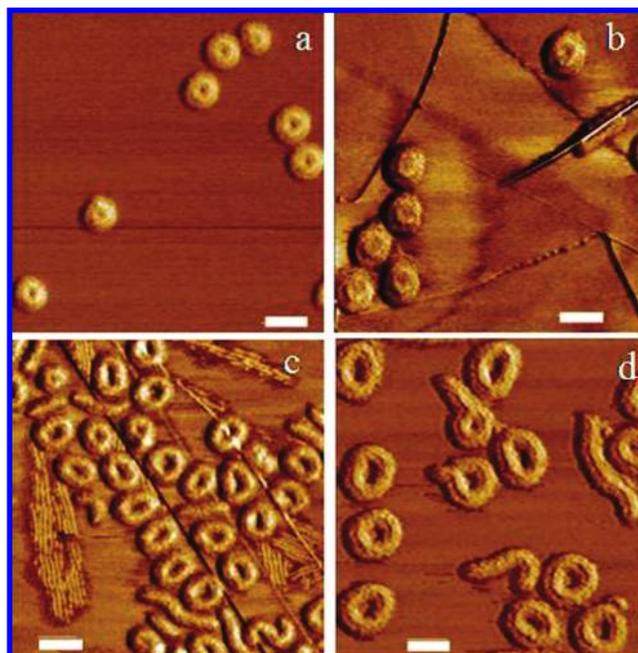


**Figure 4.** Evolution of the SEC chromatogram of the cyclohexane-soluble fraction of cyclic PS comb (sample C-2-100) recovered at decreasing temperatures in the range of 20–18 °C.

from chain dimerization. Besides linear dimers, the peak position suggests the possible formation of bicyclic, tadpole, and cyclic dimers, Scheme 3.

Deconvolution of the main SEC peak attributed to cyclic gives as a first estimate a cyclization yield in the range of 65–70%; see Table 1. As will be shown later, these values are higher than those directly measured by AFM imaging on the corresponding cyclic combs. This could be ascribed to the coelution of low molar mass linears with cyclics.

**Synthesis of Macrocyclic PS Combs.** The synthesis of PS combs by grafting living polystyrene onto PCEVE chains has been thoroughly studied in our group in recent years.<sup>22–24</sup> One interesting advantage of this technique relies on the capacity to control the dimensions and architecture of the PCEVE chains and the size of the PS grafts since both are prepared by living polymerization techniques. In addition, the good efficiency and selectivity of the coupling reaction allows the precise design of comb polymers having the same architecture as the initial polymer backbone, with a high density in PS grafts. This strategy was applied here to convert the cyclic copolymers **5** into the corresponding cyclic combs **6**. In order to achieve a high grafting density, the living polystyrene was added in slight excess with respect to the CEVE units (1.2 equiv). The comb copolymer was separated from the unreacted PS by selective precipitation in an heptane/cyclohexane mixture. The SEC chromatogram of a cyclic PS comb is shown in Figure 2. It closely reflects the SEC profile of the cyclized ABC copolymer, Figure 1, except that all peaks are shifted toward much higher molar masses. Again the presence of peak shoulders attributed to the formation of linear combs from the remaining linear ABC precursor as well as to various other types of dimeric combs is observed. These results are clearly confirmed by tapping mode AFM



**Figure 5.** AFM phase images on HOPG of cyclic polystyrene combs obtained from ABC precursors with central PCEVE B block of increasing  $\overline{DP}_n$  and/or with different PS graft lengths, (a) C-1-100, (b) C-1-170, (c) C-2-100, (d) C-3-170, cyclic comb fractions recovered by SEC fractionation (scale bars, 100 nm).

analysis of solid deposits of the PS combs obtained by casting their THF solution on HOPG.

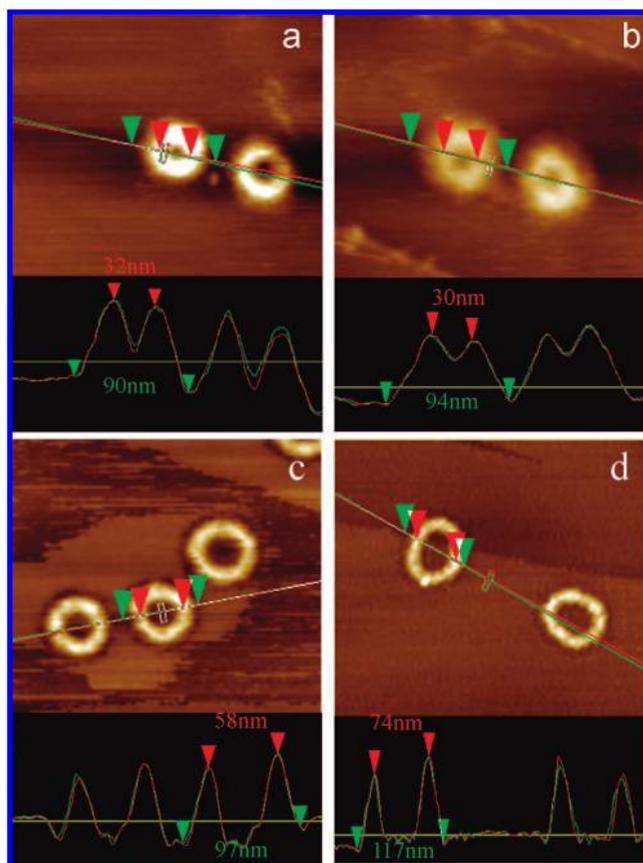
The AFM picture of a crude comb sample is presented in Figure 3a. The image shows single molecules isolated on the surface with ring structures corresponding to macrocyclic combs as well as a fraction of linear combs likely formed from uncyclized PCEVE precursors. In addition, we can also notice the formation in small proportions of comb dimers corresponding to linear ( $L_D$ ), cyclic ( $C_D$ ), tadpole ( $T_D$ ), and eight-shape bicycles ( $B_D$ ); see Figure 3b. Their possible mechanism of formation is also illustrated in Scheme 3. The linear structures are believed to result from the presence of some BC and more likely AB diblock copolymers in admixture with the ABC precursor rather than from a low efficiency of the cyclization step. Diblock copolymer formation can be attributed to transfer and/or termination reactions during the vinyl ethers cationic copolymerization. Yields in the target ring polymers were estimated directly from AFM images by counting the different comb architectures. They are in the range of 50–60%, which is slightly lower than cyclization yields estimated (around 65–70%) by SEC (Table 1). This may be explained by the coelution of a small fraction of low molar mass linears with the cyclics.

Purification of the cyclic combs was partly achieved by preferential precipitation of the various dimers and linear combs by slowly decreasing the temperature of their cyclohexane solution. As may be seen on the SEC chromatograms, Figure 4, the shoulder and small peak of linear and dimeric structures, respectively, are suppressed when incrementally decreasing the temperature from 20 to 18 °C, whereas the SEC peak of cyclic combs gets narrower and shifts to slightly higher elution volumes. The precipitation of linear combs at higher temperature than cyclics of same molar masses can be related to the difference in their  $\Theta$  temperature as already reported for linear and cyclic polystyrenes.<sup>31</sup> As shown in AFM images presented

**Table 3.** Characteristic Dimensions and Parameters of Linear (L) and Cyclic (C) PCEVE-*g*-PS Combs

combs <sup>a</sup>	$\bar{M}_n \times 10^{-5}$ <sup>b</sup>	$M_p \times 10^{-5}$ <sup>b</sup>	$\bar{M}_w/\bar{M}_n$	$M_{pc}/M_{pn}$	$\bar{M}_w \times 10^{-5}$ <sup>c</sup>	$R_g$ (nm) <sup>d</sup>	$\langle R_{gC} \rangle^2 / \langle R_{gL} \rangle^2$	$R_h$ (nm) <sup>e</sup>	$R_g/R_h$ <sup>f</sup>	$R_{hC}/R_{hL}$ <sup>f</sup>
L-1-100	7.90	10.01	1.17	0.74	60.05	38.8	0.53	34.1	1.04	0.90
C-1-100	6.70	7.40	1.13		58.30	28.4		30.5	0.93	
L-1-170	8.80	11.43	1.12	0.84	68.60	37.4	0.62	35.5	0.95	0.92
C-1-170	7.99	9.68	1.16		64.60	29.6		32.6	0.90	
L-2-100	11.22	15.20	1.15	0.72	79.00	54.1	0.48	40.0	1.35	0.90
C-2-100	9.42	10.88	1.12		75.40	37.1		35.5	1.04	
L-3-170	17.17	21.59	1.17	0.74	119.00	71.7	0.49	48.5	1.47	0.88
C-3-170	12.63	15.98	1.19		112.00	49.7		43.0	1.15	

<sup>a</sup> Refs of linear (L) and cyclic (C) samples (see Table 1) with  $\overline{DP}_n$  of the PS grafts,  $\bar{M}_n = 10\,700$ , PDI = 1.04, and PS<sub>170</sub>,  $\bar{M}_n = 17\,950$ , PDI = 1.03. <sup>b</sup> Determined by SEC in THF on the basis of PS standards. <sup>c</sup> Measured by SLS with a refractive index increment ( $dn/dc$ ) of 0.18. <sup>d</sup> Measured by SEC/SLS in THF. <sup>e</sup> Measured by DLS in THF. <sup>f</sup> Measured at 20 °C in THF.

**Figure 6.** AFM section analysis of isolated cyclic PS combs corresponding to samples a–d of Figure 5.

in Figure 3c it is also possible to significantly enrich the cyclic comb fraction, up to about 80%, by SEC fractionation. The influence of both the PCEVE and the PS graft  $\overline{DP}_n$ 's on the ring size, the ring section, and the central cavity dimension is illustrated in Figures 5 and 6 on samples in which either the backbone  $\overline{DP}_n$  and/or the PS grafts length are different. The corresponding ring parameters are collected in Table 2. As may be seen, the ring diameter, measured at the middle of the ring section, corresponds to a almost fully stretched PCEVE backbone. The ring section increases with the  $\overline{DP}_n$  of the PS grafts in agreement with a close packing of PS branches around the backbone. For the longer PS grafts the central cavity is partly or even almost completely filled (Figure 5, parts c and d).

**Ring Reopening of the Cyclic Combs.** The cyclization process through intramolecular formation of acetal linkages, Scheme 2, allows reopening the rings via quantitative acetal hydrolysis in acidic media, as confirmed by SEC and AFM imaging, Figure

**Figure 7.** AFM image of cyclic combs after treatment in acidic media.

7. This permits us to get cyclic and linear combs with the same constitutional parameters (backbone  $\overline{DP}_n$ , number and length of PS branches), which are very useful models for direct comparison of the linear and cyclic properties. The SEC chromatograms of the corresponding comb polymers are shown in Figure S2 as Supporting Information, whereas the evolution of the comb molar mass and gyration radius as a function of the elution volume of linear and cyclic homologues shown in Supporting Information Figure S3. The ratio between the SEC apparent peak molar mass of the cyclic and linear combs ranges from 0.72 to 0.84 depending on the comb parameters (backbone and PS lengths). The more compact cyclic comb (C-1-170), with no detectable central cavity, shows the smallest difference with its linear analogue. This can be tentatively explained by a behavior closer to a compact sphere than to a ring. The main characteristics of linear and cyclic PS combs, including apparent and absolute molar masses, hydrodynamic radius, and radius of gyration in THF, are collected in Table 3. The  $\langle R_{gC} \rangle^2 / \langle R_{gL} \rangle^2$  and  $R_{hC}/R_{hL}$  values of the PS combs are close to 0.5 and 0.9, respectively, in very good agreement with data previously determined for linear and cyclic polystyrenes.<sup>31,32</sup> This shows that the architecture of the chain is still largely predominating over other parameters in comb structures. This could be explained by the fact that the original linear and cyclic polymers have been magnified to the same extent by the grafting process, thus preserving their original characteristics.

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**Supporting Information Available:** <sup>1</sup>H NMR of linear ABC triblocks, SEC chromatograms of cyclic and linear PS combs, as well as the SEC–light scattering dependence of their molar mass and radius. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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