Linear and Semicyclic Amphiphilic Diblock Copolymers. 1. Synthesis and Structural Characterization of Cyclic Diblock Copolymers of Poly(hydroxyethyl vinyl ether) and Linear Polystyrene and Their Linear Homologues

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ABSTRACT: We recently proposed a new method allowing the controlled synthesis of ring-shaped polymers with predictable molar masses and narrow molar mass distribution. The cyclization is based on a unimolecular "end-to-end" coupling reaction of an heterodifunctional linear polymer precursor. In this paper, this methodology is applied to the synthesis of semicyclic block copolymers comprising a cyclic hydrophilic block on which a linear hydrophobic polymeric tail is attached, i.e., a cyclic diblock copolymer of poly(hydroxyethyl vinyl ether) and linear polystyrene. The general strategy for the synthesis involves three main steps: (i) preparation of a linear α-acetal-γ-styrenyl-poly(chloroethyl vinyl ether-*block*-styrene) precursor, (ii) intramolecular coupling involving the activation and reaction of the two complementary functions under high dilution, yielding the cyclized poly(CEVE) block, and (iii) substitution by hydroxy functions of the chloro side groups of poly(CEVE) block in order to form the amphiphilic semicyclic diblock copolymer. The corresponding linear diblock copolymer, with the same block length, $\overline{DP}_n$, and molar mass distribution, was simultaneously obtained using steps i and iii. The synthesis and characterization of these new diblock copolymers of controlled dimensions is described.

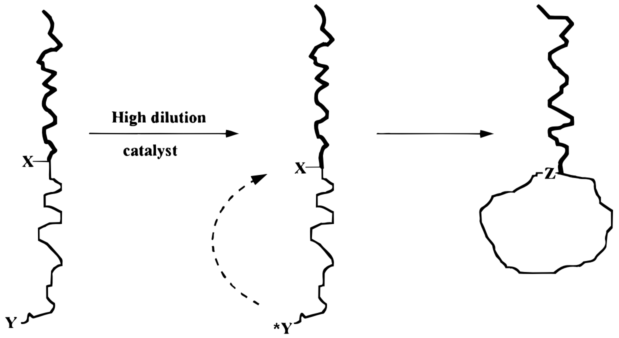
Introduction

There is presently a strong interest in exploring the role of chain topology on the physicochemical properties of macromolecules, as evidenced by the increasing number of works dealing with the synthesis and study of polymers with complex chain architecture. Stars,[1] dendrimers,[2] and rings[3] of well-controlled structure and dimensions are representative of this new generation of macromolecules.

We recently proposed[4,5] a new method allowing the controlled synthesis of ring-shaped polymers with predictable molar masses and narrow molar mass distribution. The cyclization is based on a unimolecular "end-to-end" coupling reaction. The encounter probability of the two end functions of a single chain depends mainly on the distance between these two antagonist functions and is not directly affected by concentration, contrarily to interchain coupling. Therefore, the cyclization reaction remains extremely efficient at the very high dilution conditions used to favor intramolecular coupling versus intermolecular condensation. The method involves first the preparation of a linear polymer, with controlled $\overline{DP}_n$, possessing two complementary reactive functions, by living-type polymerization techniques. This precursor is then cyclized under high dilution by the selective reaction of one function with the complementary one (see Scheme 1). Depending on the structure of the precursor, in particular the location and the number of pairs of complementary reactive functions, mono-,[4−7] bi-,[8] and tricyclic polymers[9] have been synthesized.

In addition to the specific properties of cyclic polymers which mainly result from the absence of chain end effect and from a hydrodynamic volume lower than that of the corresponding linear species, it was shown that macromolecules with tricyclic architecture can complex organic salts and large molecules;[10,11] the role of chain topology in that process is not yet well-understood.

Scheme 1



Besides, the influence of the ring architecture on the chain organization and on the associative properties has not yet been studied in detail. In the case of block copolymers, in particular those comprised of amphiphilic segments, we may expect that cyclic macromolecules will behave quite differently from the corresponding linear ones.[12] A series of studies has been recently implemented in this domain to synthesize well-defined linear and cyclic amphiphilic block copolymers, in order to investigate and compare their bulk and solution properties.

This paper reports on the synthesis and characterization of a first series of diblock copolymers of controlled dimensions, comprising by a cyclic hydrophilic block on which a linear hydrophobic polymeric tail is attached (see Scheme 1).

Results and Discussion

The general strategy for the synthesis of amphiphilic semicyclic diblock copolymers, specifically, cyclic diblock copolymers of poly(hydroxyethyl vinyl ether) and linear polystyrene, involves three main steps:

(i) preparation of a linear α-acetal-γ-styrenyl-poly(chloroethyl vinyl ether-*block*-styrene) precursor, i.e., a

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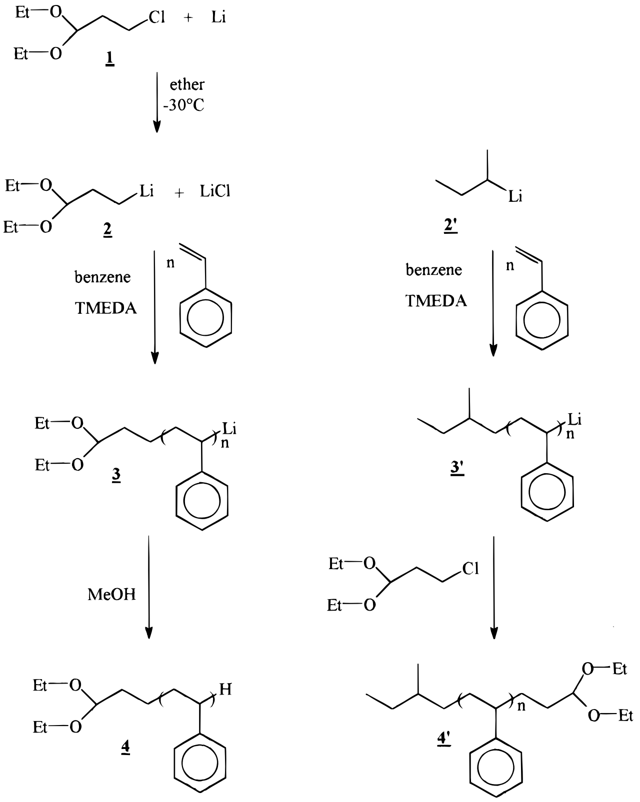
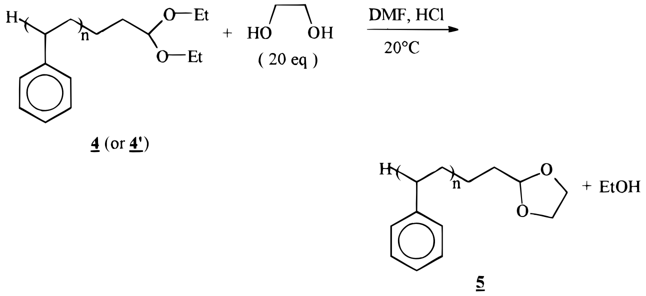
Scheme 2



Scheme 3



diblock copolymer with two functions of complementary reactivity, one attached to the end of the poly(CEVE) block (noted α), the other located between the two blocks (noted γ), as a side group;

(ii) intramolecular coupling involving the activation and reaction of the two complementary functions under high dilution, to yield the cyclized poly(CEVE) block; and (iii) substitution by hydroxy functions of the chloro side groups of poly(CEVE) blocks in order to form the amphiphilic semicyclic diblock copolymers.

The corresponding linear diblock copolymers, with the same block lengths $\overline{DP}_n$ and molar mass distribution, were obtained using steps i and iii.

In this paper we report on the above synthetic procedure for the preparation of an amphiphilic cyclic diblock copolymer of poly(hydroxyethyl vinyl ether) and linear polystyrene with special focus on the selectivity of the various reactions successively involved. These are examined on the basis of a detailed characterization of the various polymer intermediates and of the final amphiphilic linear and semicyclic diblock copolymers.

(i) Preparation of Linear α-Acetal-γ-styrenyl-poly(chloroethyl vinyl ether-*block*-styrene)s. (a) Synthesis of Linear α-Diethyl Acetal Polystyrenes. These were prepared by living anionic polymerization techniques, according to two different pathways (Scheme 2).

Pathway I: The α-diethyl acetal head group is introduced from initiation of the styrene polymerization by 3-lithiopropionaldehyde diethyl acetal, as already described.[4,5]

Pathway II: Living polystyryllithium, resulting from initiation of the styrene polymerization with *sec*-butyllithium, is deactivated by 3-chloropropionaldehyde diethyl acetal. Recent studies have shown that chloroalkyl derivatives bearing an heteroatom able to complex with the lithium cation can selectively functionalize polystyryllithium chains through termination, without any detectable contribution of chain coupling through lithium−halogen exchange.[13]

As indicated in Table 1, a good agreement between experimental and theoretical $\overline{DP}_n$, as well as a narrow molecular weight distribution (MWD; $I \leq 1.1$), is observed by either route. In the case of pathway II, the functionality of chain ends can be calculated from the intensity ratio of methyl protons of *sec*-butyl head groups (6 H, $\delta = 0.8$ ppm) and of the methine acetal proton (1 H, $\delta = 4.45$ ppm). This amounts—within experimental error—to approximately 0.90−0.95 acetal group per PS chain.[13] Since in the second pathway styrene polymerization proceeds through quantitative lithioacetal initiation, we may assume that the acetal functionality is close to 1.

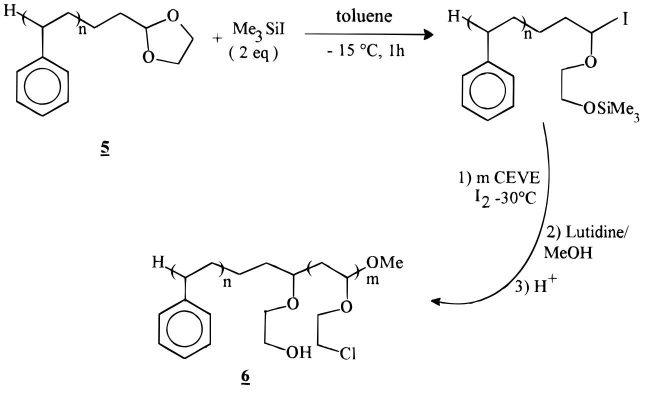
(b) Transformation of the PS α-Diethyl Acetal End into an α-Cyclic Acetal End. To introduce into the polymer chain a protected hydroxy group, to be utilized later to anchor a styrenyl group (see Scheme 5), the PS α-diethyl acetal was transformed into a α-1,2-ethanediol acetal by transacetalization (Scheme 4). This was achieved by reaction of the α-diethyl acetal PS with an excess of ethylene glycol in slightly acidic medium. The ^{1}H NMR spectra of an α-diethyl acetal PS before and after the transacetalization are shown in Figure 1. The complete disappearance of the proton signals of ethoxy groups [g (6 H), $\delta = 1.25$ ppm; f (4 H), $\delta = 3.6$ ppm; and e, (1 H) $\delta = 4.45$ ppm], accompanied by the appearence of signals relative to protons of α-1,2-ethanediol acetal [f′ (4 H), $\delta = 3.9$ ppm; e′ (1 H), $\delta = 4.75$ ppm], confirms the group exchange. Titration of the acetal methylenic protons supports that the modification of the PS ends is quantitative.

Table 1. Characteristics of Linear α-Diethyl Acetal Polystyrenes[a]

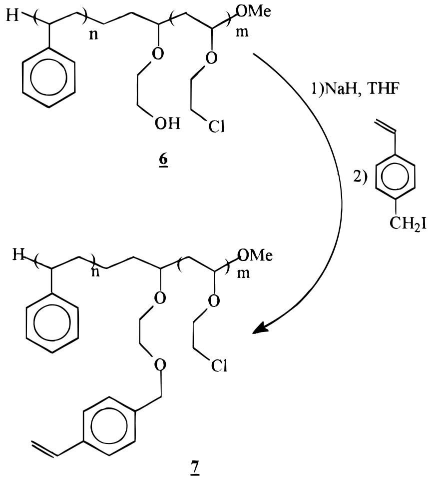
sample	pathway	$\overline{DP}_n$(theory)[b]	$\overline{DP}_n$(exptl)[c]	$\bar{M}$(exptl)[d]	$\bar{M}_w/\bar{M}_n$	acetal ends[e]/ *sec*-butyl ends
1	II	10	11	1300	1.13	0.94
2	I	12	16	1800	1.10	
3	I	15	17	2000	1.08	
4	II	35	38	4100	1.03	0.90
5	I	50	53	5600	1.08	

[a] Polymerization conditions: room temperature; reaction time, 1−2 h; solvent, benzene. [b] Calculated from the ratio [monomer]/[initiator]. [c] Determined by ^{1}H NMR from the ratio of protons -C_6H_5/-$CH(OCH_2CH_3)_2$ (pathway I) or from the ratio of protons -C_6H_5/-$CH(CH_3)CH_2CH_3$ (pathway II). [d] Determined by SEC (PS calibration). [e] Determined by ^{1}H NMR from the ratio of protons -$CH(OCH_2CH_3)_2$/-$CH(CH_3)CH_2CH_3$.

Scheme 4



Scheme 5



(c) Synthesis of Linear α-Acetal-γ-hydroxy-poly(chloroethyl vinyl ether-*block*-styrene)s. The initiation of the CEVE cationic polymerization was achieved, as previously reported,[4,14] by transformation of an α-1,2 ethanediol acetal PS end group into α-iodo ether in the presence of trimethylsilyl iodide (TMSI; see Scheme 4). The CEVE polymerization was then triggered by adding the monomer and a catalytic amount of I_2 or $ZnCl_2$. After 2−4 h, although the CEVE conversion was generally not complete, the polymerization system was deactivated by adding a solution of methanol and 2,6-lutidine, thus leading to the α-acetal-γ-(trimethylsilyl)oxy diblock poly(CEVE-*b*-S). The (trimethylsilyl)oxy group was readily hydrolyzed by acidic treatment of the polymer, yielding a γ-hydroxy function between the two blocks.

The SEC chromatogram and the ^{1}H NMR spectrum of a linear α-acetal-γ-hydroxy-poly(CEVE-*b*-S) diblock copolymer, sample 3b in Table 2, are shown in Figures 2 and 3, respectively.

As it may be seen from Figure 2, copolymers with narrow molecular weight distributions are obtained ($I \leq 1.10$). The increase of the SEC molar masses, with respect to the PS chain precursor one, as well as the absence of any detectable signal corresponding to unreacted PS, suggests that initiation of the CEVE polymerization from the 1,2-ethanediol acetal termini of PS is almost quantitative. The linear α-acetal-γ-styrenyl-poly(CEVE-*b*-S) exhibits a tail at low $\bar{M}_n$: it corresponds to a small fraction of CEVE homopolymer (1−5%), resulting from side initiation due to the presence of HI generated from TMSI hydrolysis, indicating that the CEVE polymerization is also relatively well controlled. However, coupling of a small fraction of chains, peak tail at high $\bar{M}_n$ on the SEC trace (around 1−5%), sometimes occurred, likely during the termination of active ends by methanol/lutidine,[15] and could not be systematically avoided.

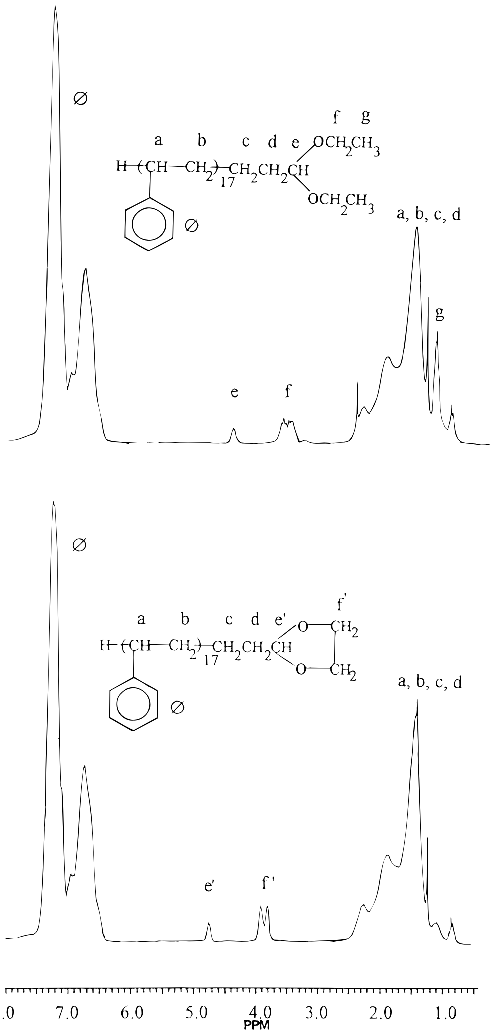


Figure 1. 200 MHz ^{1}H NMR spectra of a linear α-diethyl acetal PS (a) and a 1,2-ethanediol acetal PS (b). Solvent, $CDCl_3$.

Table 2. Characteristics of α-Acetal-γ-hydroxy-poly(chloroethyl vinyl ether-*block*-styrene)s[a]

sample	$\overline{DP}_n$(exptl)[b] of PS block	$\overline{DP}_n$(exptl) of PCEVE block[c]	$\bar{M}_n$-(theory)[c]	$\bar{M}_n$-(exptl)[d]	$\bar{M}_w/\bar{M}_n$
1	9	15	2724	2640	1.06
2	17	14	3394	3800	1.09
3a		15	5676	6050	1.04
3b	38	27	6948	6300	1.10
3c		46	8962	8550	1.02

[a] Polymerization conditions: temperature, −30 °C; reaction time, 2−4 h; solvent, toluene. [b] Determined by ^{1}H NMR (see legend of Table 1). [c] Calculated by ^{1}H NMR from the ratio CEVE/PS units. [d] Determined by SEC (PS calibration); $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ are apparent values.

The characteristics of various linear ambifunctional diblock copolymers are summarized in Table 2.

(d) Anchoring of the Styrenyl Group at the γ-Position. The reaction pathway is given Scheme 5. The γ-hydroxy function of the block copolymer was firstly transformed into alkoxide, in the presence of sodium hydride, and then reacted with a large excess of (iodomethyl)styrene in order to achieve the quantitative anchorage of the styrenyl function. The procedure

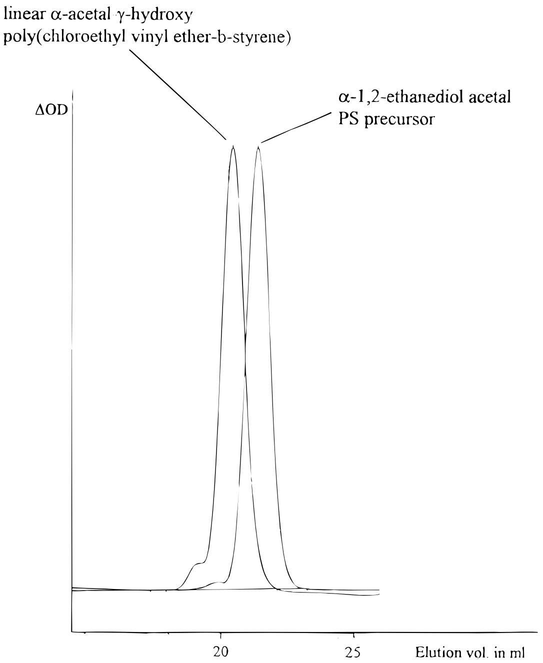


Figure 2. GPC curves of a linear α-acetal-γ-hydroxy-poly(chloroethyl vinyl ether-*block*-styrene) of $\bar{M}_n = 6300$ and its α-ethanediol acetal PS precursor of $\bar{M}_n = 4100$.

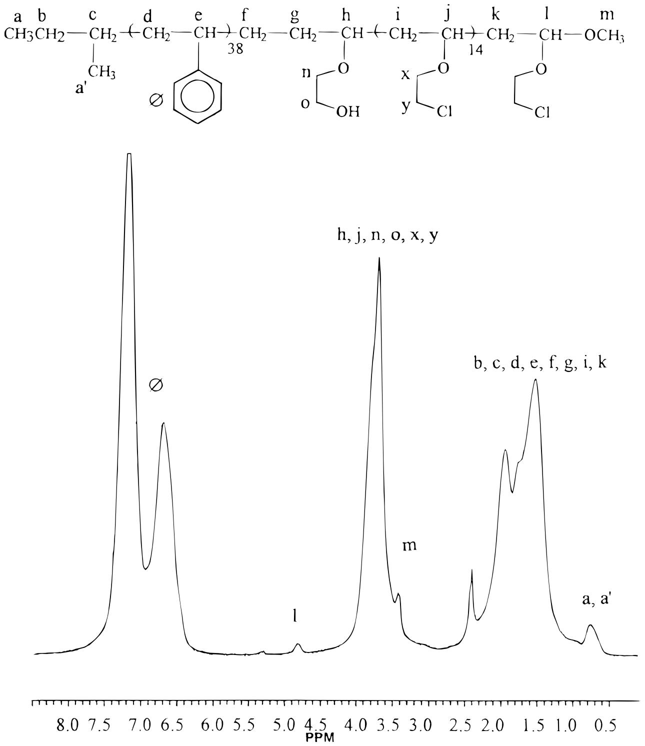


Figure 3. 200 MHz ^{1}H NMR spectrum of a linear α-acetal-γ-hydroxy-poly(chloroethyl vinyl ether-*block*-styrene). Solvent, $CDCl_3$.

was eventually repeated twice when the proportion of styrenyl group, as determined by ^{1}H NMR, was less than expected.

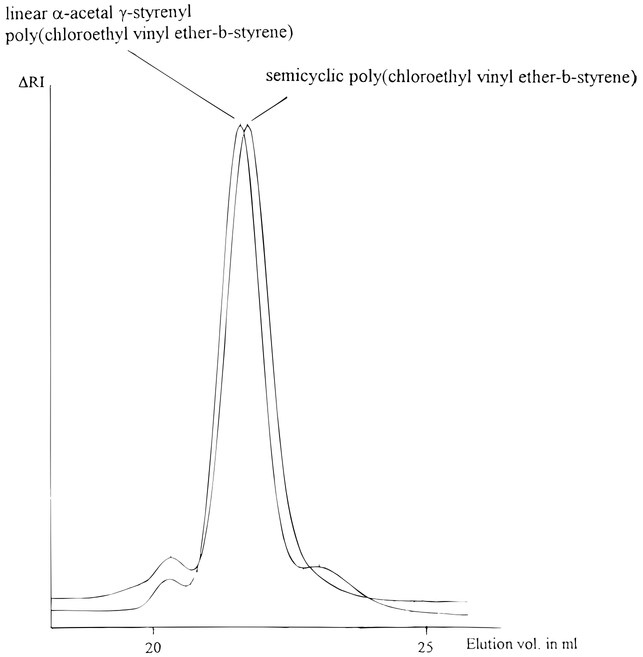


Figure 4. GPC curves of a α-acetal-γ-styrenyl-poly(chloroethyl vinyl ether-*block*-styrene) ($\bar{M}_n = 6300$) before and after the cyclization of the poly(CEVE) block.

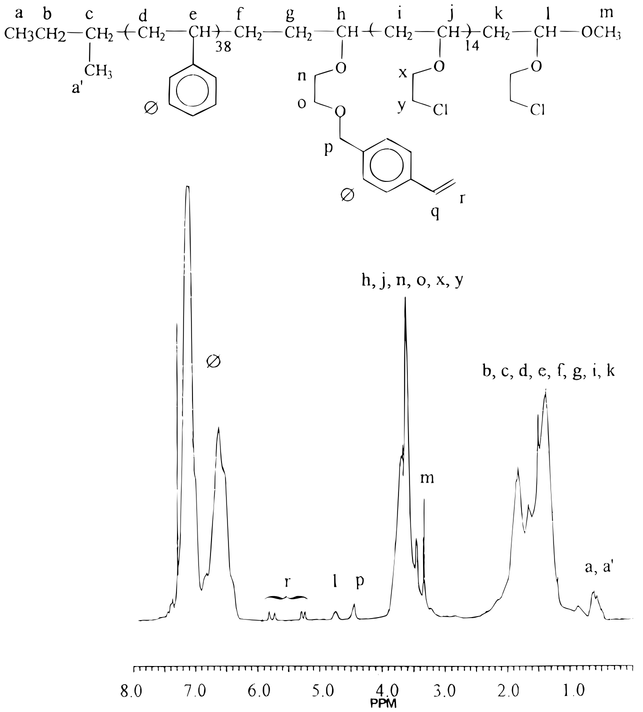


Figure 5. 200 MHz ^{1}H NMR spectrum of a linear α-acetal-γ-styrenyl-poly(chloroethyl vinyl ether-*block*-styrene). Solvent, $CDCl_3$.

The SEC chromatogram and the ^{1}H NMR spectrum of a linear α-acetal-γ-hydroxy-poly(CEVE-*b*-S) are shown in Figures 4 and 5, respectively. The characteristic signals of the styrenyl group [r (2 H), $\delta = 5.25$ and $\delta = 5.75$ ppm] and the signal of benzylic protons [p (2 H), $\delta = 4.45$ ppm] are observed. On the basis of peak integration of the acetal proton [l (1 H), $\delta = 4.75$ ppm] and of protons characteristic of the styrenyl group (methylene signal r for exemple), we may conclude that the ratio between acetal and styrenyl groups is very close to 1, in agreement with the structure expected for linear precursors of semicyclic diblock copolymers.

(ii) Cyclization Procedure. (a) Cyclization by "Cationic Activation" of the α-Acetal End with $TiCl_4$. The cyclization was achieved under very high dilution conditions[4,5] by the intramolecular reaction of the cationized α-acetal end of the poly(CEVE) block onto the unsaturation of the γ-pendant styrenyl group of the diblock copolymer precursor (see Scheme 5). Typically, a methylene dichloride solution of the linear α-acetal-

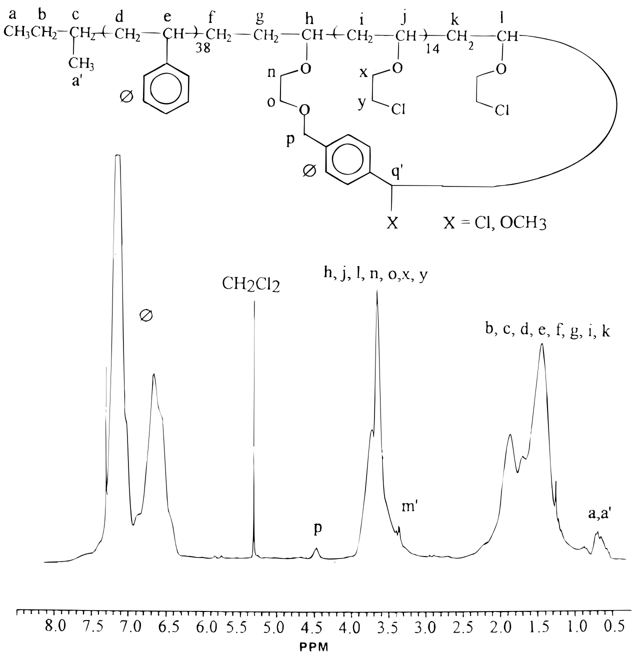


Figure 6. 200 MHz ^{1}H NMR spectrum of a semicyclic poly(chloroethyl vinyl ether-*block*-styrene). Solvent, $CDCl_3$.

γ-styrenyl-poly(CEVE-*b*-S) was added dropwise to a large volume of methylene dichloride containing traces of water and/or ethanol and a strong Lewis acid, $TiCl_4$. This procedure allows the "activation" of the α-acetal termini, which can then react onto the styrenyl functions.

The proposed[8] reaction pathway involves first the formation *in situ* of hydrogen halide by partial hydrolysis, or ethanolysis, of the Lewis acid and second the cationation of the acetal function by the $HCl-TiCl_4$ acid complex, leading to a highly reactive carbocationic-like end group, which rapidly adds on to the styrenyl unsaturation to yield to a new species, inactive under the present reaction conditions. Finally, after complete addition of the linear precursor to the cyclization medium, the system was neutralized by addition of a solution of methanol and ammonia.

The characteristic ^{1}H NMR spectrum of a semicyclic poly(CEVE-*b*-S) is shown in Figure 6. The absence of signals of the styrenyl unsaturation [r (2 H), $\delta = 5.25$ and $\delta = 5.75$ ppm], as well as of the acetal [l (1 H), $\delta = 4.75$ ppm], indicates that the two complementary reactive functions have been quantitatively consumed during the cyclization process.

As it may be seen in Figure 4, the polydispersity of the semicyclized copolymer remained as narrow ($I \leq 1.10$) as that of the linear precursor.

Some characteristics of linear and semicyclic poly(CEVE-*b*-S)s are given in Table 3.

(b) Determination of $\langle G_{\mathrm{theor}} \rangle$. As predicted by theory of cyclic polymers,[4,16,] the semicyclized copolymers are characterized by a smaller hydrodynamic volume than that of the linear ones. The experimental $\langle G \rangle$ values, $\langle G_{\mathrm{exptl}} \rangle$, for the semicyclic polymers, obtained by SEC analysis from the ratio $M_p(c)/M_p(l)$ are in the range 0.92−0.97. These values are higher than those found for pure cyclic PS ($\langle G_{\mathrm{exptl}} \rangle = 0.78$)[6] and cyclic poly(CEVE) ($\langle G_{\mathrm{exptl}} \rangle = 0.82$),[17] as could be expected from the semicyclic structure of the block copolymers. Indeed, $\langle G_{\mathrm{exptl}} \rangle$ varies in accordance with the relative size of the poly(CEVE) cycle and the PS tail: the higher the relative size of the cyclic poly(CEVE) block, the lower the experimental $\langle G \rangle$ value.

Assuming, as a rough approximation, a simple linear variation of $\langle G \rangle$ values with the relative fractions of the PS (F_{PS}) and poly(CEVE) (F_{PCEVE}) blocks, we may write

$$\langle G \rangle = \langle G°_c \rangle (F_{PCEVE}) + \langle G°_l \rangle (F_{PS}) \tag{1}$$

where $\langle G°_c \rangle = 0.82$, $\langle G°_l \rangle = 1$, and the fractions of the two blocks are expressed by

$$F_{PS} = \overline{DP}_n(PS)/[\overline{DP}_n(PCEVE) + \overline{DP}_n(PS)]$$

$$F_{PCEVE} = \overline{DP}_n(PCEVE)/[\overline{DP}_n(PCEVE) + \overline{DP}_n(PS)]$$

The calculated $\langle G \rangle$ values obtained from eq 1 are in relatively good agreement with the observed $\langle G_{\mathrm{exptl}} \rangle$ values (see Table 3), suggesting that the ratio of hydrodynamic volumes of the semicyclic and the linear block copolymers may be considered to a first approximation as the sum of individual contributions of the cyclic and linear segments.

(iii) Preparation of Amphiphilic Semicyclic Poly(hydroxyethyl vinyl ether-*block*-styrene). Chloroethyl vinyl ether is a monomer of specific interest in macromolecular synthesis since it can be polymerized by a living mechanism to yield a polymer containing labile chlorides, allowing the anchorage of a large number of side groups through nucleophilic substitutions.[10,11] Indeed, the chloro functions can be quantitavely replaced without any noticeable influence of side reactions on the $\overline{DP}_n$ and MWD of the chains.

The substitution of the chloro functions by hydroxyls was performed in a two-step process (see Scheme 7).

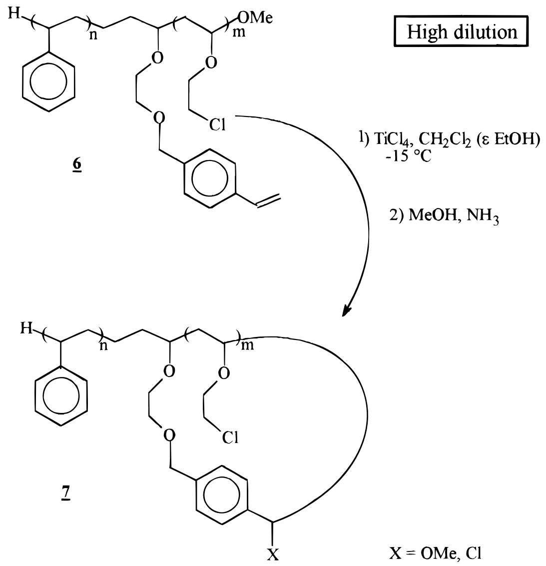
(a) Nucleophilic Substitution of the Chloro Functions in the Presence of Potassium Acetate. This was achieved with an excess of potassium acetate in the presence of a small amount of tetrabutylammonium salt (bromide or hydrogen sulfate). The ^{1}H NMR spectra of a semicyclic poly(AcEVE-*b*-S) obtained after the substitution of chloride by acetyl functions, presented in Figure 7, can be compared to that of poly(CEVE-*b*-S), in Figure 6. The modified copolymer is characterized

Table 3. Characteristics of Linear and Semicyclic Poly(chloroethyl vinyl ether-*block*-styrene)s Obtained by "End-to-End" Unimolecular Cyclization

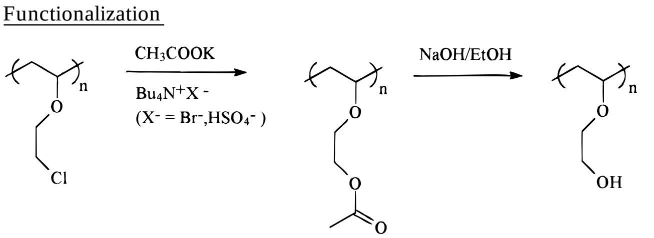
$\overline{DP}_n$(exptl)[a]							
PS block	PCEVE block	architecture	M^{pb}	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\langle G_{\mathrm{exptl}} \rangle^c$	$\langle G_{\mathrm{theor}} \rangle^d$
	15	linear	6235	6050	1.04	0.97	0.95
		cyclic	6070	6000	1.06		
38	27	linear	7150	6300	1.10	0.95	0.93
		cyclic	6800	6750	1.06		
	46	linear	8900	8550	1.02	0.92	0.90
		cyclic	8150	7650	1.09		

[a] See sample 3, Table 2. [b] Apparent peak molecular weight determined by SEC (PS calibration); $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ are apparent values. [c] $\langle G_{\mathrm{exptl}} \rangle = M_p(c)/M_p(l)$. [d] See text.

Scheme 6



Scheme 7



by two new signals corresponding to the methyl protons CH_3COO [z (3 H), $\delta = 2.1$ ppm] and the methylene CH_2-OCO [y′ (2 H), $\delta = 4.2$ ppm]. Titration of the acetyl group with respect to the vinyl ether units supports a complete substitution of the chloride.

(b) Generation of Side Hydroxyls. These were readily obtained by hydrolysis of the acetate groups with sodium hydroxide. The ^{1}H NMR spectrum of a semicyclic poly(hydroxyethyl vinyl ether-*block*-styrene) is shown in Figure 8. The quantitative generation of hydroxyl can be established mainly from the complete disappearence of signals of the acetate groups.

A similar derivatization procedure was applied to linear poly(chloroethyl vinyl ether-*block*-styrene)s in order to prepare the corresponding linear amphiphilic diblocks of the same dimensions and chemical composition.

In conclusion, we believe that the synthesis of new amphiphilic diblock copolymers with either linear or semicyclic chain architecture, possessing controlled and predictable macromolecular parameters such as the topology and dimensions of the blocks, has been successfully achieved.

Early studies on these copolymers by SEC chromatography indicate that both the linear and semicyclic species possess a strong tendency to autoassociate in organic solvents (THF, toluene), where they remain soluble. They also exhibit interesting capacities to interact with some organic salts and molecules.

A comparative study of their behavior in bulk and in solution will be the subject of a forthcoming paper.

Experimental Section

The preparation of 3-lithiopropionaldehyde diethyl acetal, anchoring of the styrenyl groups, and typical cyclization procedures have already been described.[4-6,8]

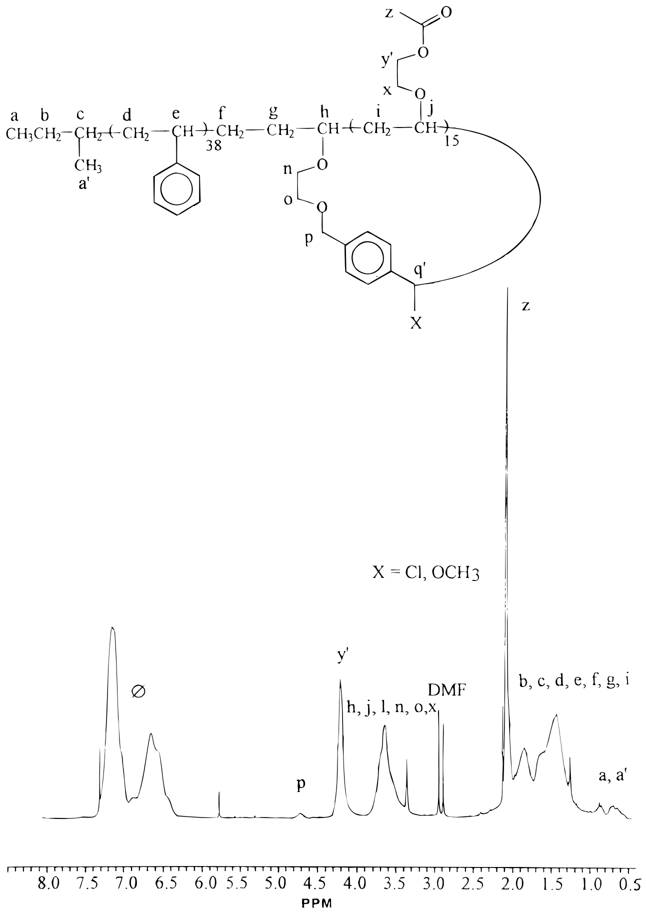


Figure 7. 200 MHz ^{1}H NMR spectrum of a semicyclic poly(acetylethyl vinyl ether-*block*-styrene). Solvent, CDCl$_3$.

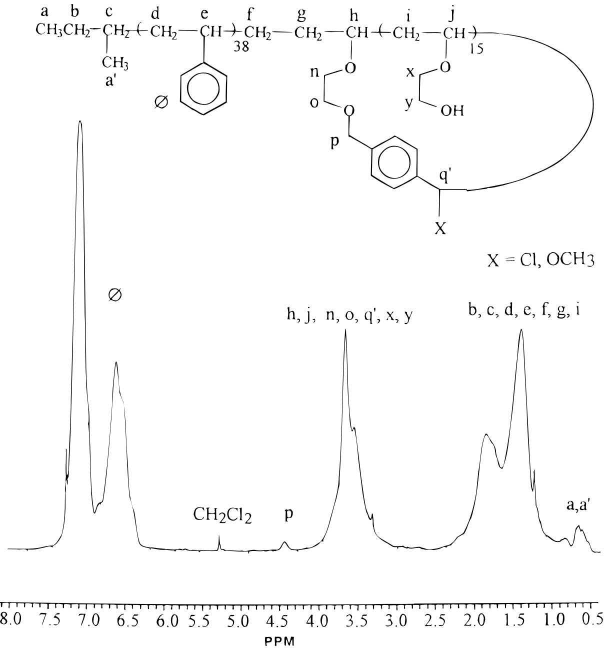


Figure 8. 200 MHz ^{1}H NMR spectrum of a semicyclic poly(hydroxyethyl vinyl ether-*block*-styrene). Solvent, CDCl$_3$.

Styrene Anionic Polymerization. The living anionic polymerization of styrene was carried out in benzene in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) at room temperature. Freshly dried solvent, styrene, and TMEDA (1.1 equiv with respect to the initiator) were successively introduced into the polymerization reactor under dry nitrogen.

Pathway I: 3-Lithiopropionaldehyde diethyl acetal prepared in diethyl ether was then added to the solution to initiate the polymerization. After 1−2 h, the living polymer was deactivated with a large excess of degassed methanol.

Pathway II: Same as pathway I procedure but with *sec*-butyllithium as initiator. 3-Chloropropionaldehyde diethyl acetal (1.2 equiv with respect to active species) was used as deactiving agent.[13] As shown by the rapid change of the medium to colorless, pathway II yields almost instantaneously transformation of PS ends.

The resulting PSs were recovered after concentration of the solution by precipitation into methanol and dried.

Chemical Transformation of the Acetal End of the PS. α-Diethyl acetal PS (15 g) dissolved in 50 mL of DMF was reacted with a large excess of ethylene glycol (20 equiv with respect to the acetal ends of PS) in the presence of 1 mL of hydrochloric acid (10 N). After about 18 h at room temperature, CH_2Cl_2 was added to the medium and the organic phase was washed three times with water, dried over $MgSO_4$, and filtered. After concentration of its solution by solvent evaporation, the modified polymer was recovered by precipitation into methanol, filtered, and dried under vacuum.

CEVE Cationic Polymerization. The acetal-modified PS was placed in a Schlenck apparatus fitted with PTFE stopcocks previouly dried under vacuum, dissolved in freshly distilled and dried toluene, and stirred several hours over calcium hydride. The filtered solution was then thermostated at −15 °C and reacted with trimethylsilyl iodide (TMSI; acetal ends/TMSI = 1:1.2) for 1 h. After the mixture was cooled at −30 °C, CEVE (amount in accordance with the theoretical $\overline{DP}_n$) and I_2 (0.1 equiv with respect to α-iodo ether) in ether solution were added successively. After 2−4 h, a solution of methanol and 2,6-lutidine was introduced to deactivate the system, and then the polymer mixture was washed with acidified methanol to hydrolyze the trimethylsilyl ether group,[8] leading to the corresponding α-acetal-*γ*-hydroxy-poly(CEVE-*b*-S) block copolymer.

The polymer was then dissolved in methylene dichloride and washed with a solution of sodium thiosulfate and twice with water. The organic phase (CH_2Cl_2) was dried over $MgSO_4$ and then filtered. The crude copolymer was recovered by partial solvent evaporation and precipitation into methanol.

Nucleophilic Substitution of Chloro Functions. Potassium acetate (3 equiv with respect to chloro functions) and tetrabutylammonium hydrogen sulfate or tetrabutylammonium bromide (0.5 equiv with respect to chloro functions) were added to a solution of either linear or semicyclic diblock copolymer in DMF. The mixture was stirred for 18 h at 80 °C. CH_2Cl_2 was added to the medium, and the organic phase was washed several times with water, dried over $MgSO_4$, and filtered. The solvent was evaporated, and the modified copolymer was dried under vacuum.

Hydrolysis of the Ester Functions. The latter polymer was dissolved in DMF and reacted with sodium hydroxide (3 equiv with respect to ester functions) dissolved in ethanol for 4 h at 80 °C. The solvent was evaporated under vacuum; the polymer residue was then washed once with a solution of hydrochloric acid in water and several times with water. The amphiphilic diblock copolymer was then filtered and dried with 1,4-dioxane evaporated under vacuum.

Polymer Characterization. The ^1H NMR spectra of the different polymers were recorded on a AC 200 MHz FT Bruker spectrometer. SEC measurements were performed in THF on a Varian apparatus equipped with refractive index/UV dual detection and fitted with three TSK columns, calibrated with PS standards. A trace of toluene added to the sample was used as the internal flow marker reference.

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