# New routes to macrocyclic polymers of controlled dimensions*

**Alain Deffieux†, Michel Schappacher and Laurence Rique-Lurbet**
*Laboratoire de Chimie des Polymères Organiques, ENSCPB, CNRS, Université Bordeaux-1, 351 Cours de la Libération, 33405 Talence Cédex, France*

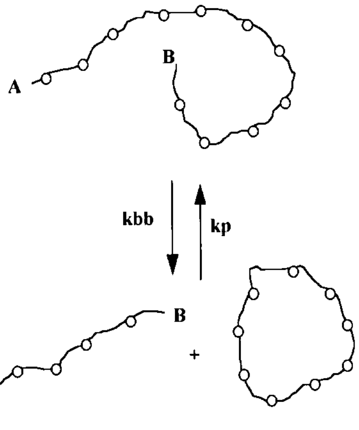
Since the early 1950s a number of theoretical studies have dealt with the prediction of the dimensions and behaviour of macrocyclic polymers. However, owing to the difficulty of synthesis, the comparison of theories with experimental data still remains restricted to a small number of macromolecules. The first cyclic polymers studied were those produced from systems in which ring–chain equilibrium exists, but it is only in the last decade that a method for the preparation of ring-shaped vinylic polymers of controlled dimensions has become available. The method involves the bimolecular end-to-end ring closure of an anionically prepared $\alpha,\omega$-difunctional linear polymer using a coupling agent. Low cyclization yields are generally observed. Besides theoretical considerations the experimental conditions which may lead to these results have been examined. In this paper a new approach to the synthesis of macrocyclic polymers with controlled dimensions is examined. In contrast to previous procedures, it involves a single unimolecular ring-closure process which is much less sensitive to the extremely low concentrations required for cyclizations. It is achieved by the direct end-coupling of an $\alpha,\omega$-heterodifunctional linear polymer precursor after the appropriate activation under high dilute conditions of one of its two end-functions. The advantages of this new approach are discussed both on theoretical and experimental grounds. Its application to the preparation of poly(vinyl ether)s, polystyrenes and poly(vinyl ether-*b*-styrene) diblock copolymers of controlled dimensions with a macrocyclic architecture is described.

**(Keywords: living polymerization; ring closure; macrocyclic polymer)**

## INTRODUCTION

The very specific role of natural and synthetic organic macrocycles in many biological and chemical processes, in particular those based on molecular recognition, has attracted in the past 25 years considerable efforts towards the design and synthesis of new organic molecules with a cyclic or pluricyclic structure[1,2]. In the same period the interest in oligomers and polymers having such ring structures has also grown. Basic theoretical aspects and the remarkable complexing capacities of low molecular weight cyclic oligomers such as calixarenes[3] and cyclodextrins[4], as well as the original physical and mechanical properties resulting from the lack of chain-ends and the topological constraints associated with the cyclic chain architecture[5–7], have been the driving forces for the rapid development of this research area.

Two main approaches are presently used for the preparation of ring polymers of controlled dimensions and narrow molecular weight distributions. The first method is based on the simultaneous formation, in some macromolecular systems, of linear and cyclic macromolecules which coexist in dynamic equilibrium (see *Scheme 1*). These ring–chain equilibria only concern polymers possessing reactive groups in the main chain, such as polycondensates, polyalkenamers and polymers formed by ring-opening polymerization of heterocycles. The polymerization of octamethylcyclotetrasiloxane[8], for example, yields a substantial fraction of macrocycles in equilibrium with linear polydimethylsiloxane. The rings are formed in a unimolecular process via intramolecular attack on a reactive group of the backbone by the active



**Scheme 1** Formation of cyclics in systems exhibiting ring–chain equilibria

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[†] To whom correspondence should be addressed

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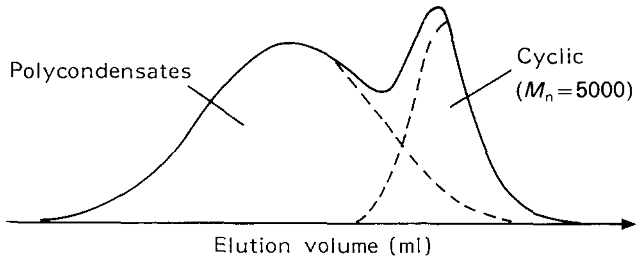
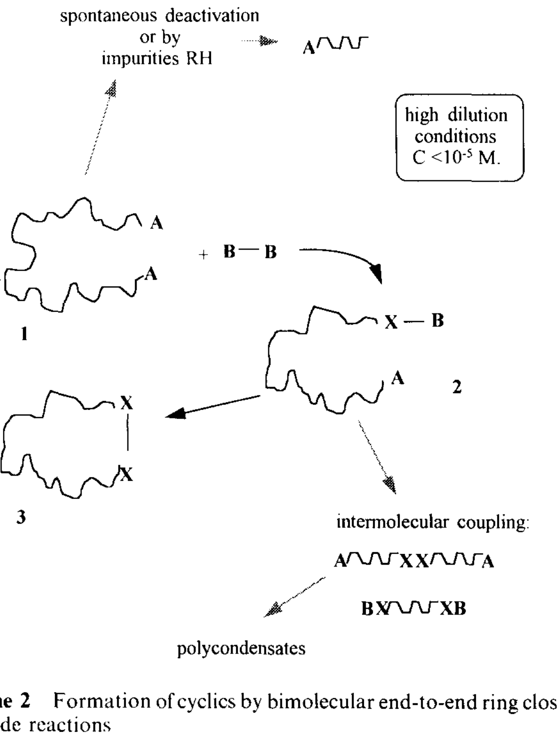


**Figure 1** Typical gel permeation chromatography (g.p.c.) curve obtained for the end-to-end cyclization of an α,ω-dicarbanionic polystyrene with a difunctional coupling agent. The dashed line highlights the distribution between cyclic and polycondensates in the crude reaction products ($\bar{M}_n$ of polystyrene = 5000)

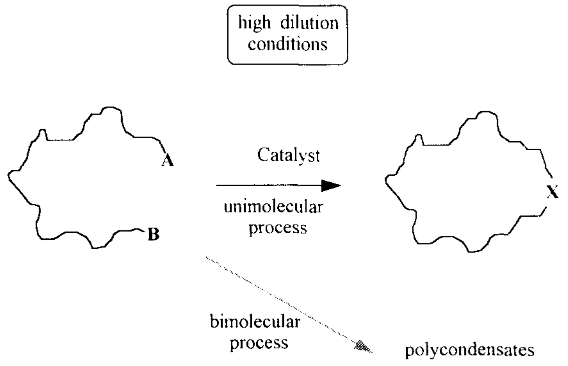
chain-end (back-biting). Although low molecular weight cyclics are predominantly formed in this process, a higher cyclic polymer fraction is also present and the distribution of ring sizes is extremely broad. To obtain pure macrocyclic polymers with controlled molecular weights and narrow polydispersities, tedious fractionation procedures are necessary. The second general method concerns polymers with carbon–carbon linkages in the backbone. It was developed in the early 1980s[9–12], when the progress in anionic polymerization allowed a good control of the structure and the chain-end functionality. The cyclization procedure involves the end-to-end ring closure of a living α,ω-dicarbanionic polymer **1** by coupling the two carbanionic ends with a difunctional electrophile under extreme dilution (see *Scheme 2*). This method yields cyclic molecules **3** of molecular weight close to that of the precursor and a fraction of polycondensates (dimers to polymers) which form at the same time by intermolecular coupling[9–16]. A typical gel permeation chromatogram of a raw polystyrene sample after end-to-end cyclization is presented in *Figure 1*. Factors which may lead to limited conversions into cyclics have recently been pointed out by Hogen-Esch *et al.*[17].



**Scheme 2** Formation of cyclics by bimolecular end-to-end ring closure and side reactions

In addition, it is worth noting that the ring closure is a 'one-pot', two-step process which successively involves a bimolecular and a unimolecular reaction. The first step is the bimolecular condensation between a polymer chain-end and one of the coupling agent functions. Though it is a common step for the cyclization and polycondensation processes (see *Scheme 2*), the selective and quantitative formation of the α,ω-heterodifunctional polymer **2** is of primary importance for the formation of the cyclic polymer. This implies the use of a chemically pure difunctional linear precursor **1** and the control of its specific monocondensation with one function of a dielectrophile[17]. The second step involves the end-to-end unimolecular cyclization reaction of **2**. This must be favoured over other (bimolecular) processes which lead to polycondensation. This is best achieved by working at very low active species concentrations and keeping them at stoichiometry. In fact, it is very difficult to respect these experimental requirements strictly. It should also be noted that the high dilution conditions required for the cyclization step are not favourable for the quantitative formation of the heterodifunctional polymer intermediate **2**. This may explain why the percentages of cyclic polymers formed are generally lower than theoretically predicted. Again, to get pure cyclic fractions it is necessary to use fractionation procedures. An exception to this general trend has been reported recently for α,ω-dilithiopoly(isoprene)[18]. High cyclization yields have been accounted for by the specific formation of triple ions leading to polymers in a precyclized form.

To overcome some of these experimental difficulties, a different approach to polymer macrocycles of controlled molecular weight (MW) and narrow MW distribution (MWD) has been investigated. The general pathway is also based on a two-step process. The first step involves the preparation by a living polymerization technique at an ordinary concentration of a heterodifunctional polymer of controlled chain dimensions and end-functions. The cyclization of heterodifunctional linear precursors is then performed in a completely separate second step at very dilute reaction conditions. It involves the reaction, after appropriate activation, of one of the active ends of the precursors with the other end-function of the same polymer chain, as illustrated in *Scheme 3*. Therefore, the ring-closure pathway proceeds via a unique unimolecular process. The application of this method to the preparation of various cyclic polymers is now described.



**Scheme 3** Formation of cyclics by direct end-to-end ring closure

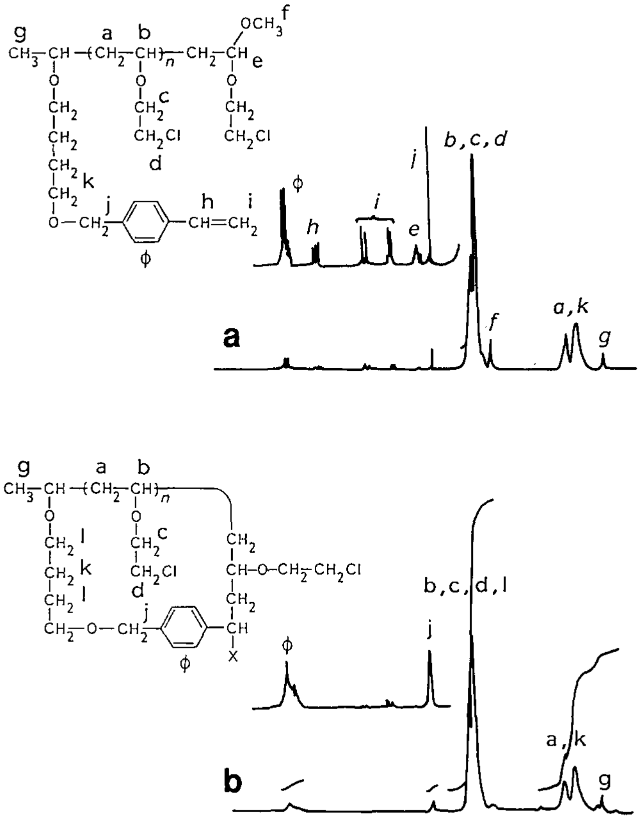


**Figure 2** $^{1}H$ n.m.r. spectra of (a) an α-styrenyl-ω-acetalpoly(CEVE) ($\overline{DP}_n = 20$) and (b) the corresponding cyclized product

## EXPERIMENTAL

The preparation of linear heterodifunctional α-styrenyl-ω-acetalpoly(chloroethyl vinyl ether)s and their cyclization procedure have already been described[19]. The preparation of linear heterodifunctional α-styrenyl-ω-acetalpolystyrenes and their cyclization procedure according to method I (see later) have also been reported[20].

### *Cyclization of α-styrenyl-ω-acetalpolystyrene by method II*

A $CH_2Cl_2$ solution of the linear α-styrenyl-ω-acetalpolystyrene (100 ml, 0.6–1 g) was placed in a dropping funnel and added dropwise (over 4 h) to a large volume of $CH_2Cl_2$ (1000 ml) containing $SnCl_4$ ($8 \times 10^{-3}$ M) maintained at 20°C under rapid stirring. After the addition was complete, the system was allowed to react for 30 min and then deactivated by adding a mixture of methanol and ammonia. The solution was finally filtered and washed and the polymer was recovered by precipitation in methanol and analysed.

### *Synthesis of linear α-styrenyl-ω-acetalpoly(styrene-*b*-chloroethyl vinyl ether)*

In a typical example, α-styrenyl-ω-acetalpolystyrene ($\bar{M}_n = 2000$; 1 g, $5 \times 10^{-4}$ mol) was dissolved in 50 ml of toluene and calcium hydride was added to the solution. After agitation for several hours, the solution was filtered under argon to eliminate $CaH_2$. After cooling the polymer solution to −40°C, trimethylsilyl iodide (TMSI) (1.2 equivalents with respect to the acetal ends), chloroethyl vinyl ether (CEVE) ($9.6 \times 10^{-3}$ mol) and $ZnCl_2$ in solution in acetone ($2 \times 10^{-5}$ mol) were added in that order. After 2 h the polymerization was terminated by adding methanol and ammonia in order to regenerate an ω-acetal at the end of the copolymer.

### *Cyclization of α-styrenyl-ω-acetalpoly(styrene-*b*-CEVE)*

This was performed according to method I[20].

### *Polymer and copolymer characterizations*

$^{1}H$ n.m.r. spectra were recorded on a Bruker AC 250. Gel permeation chromatography (g.p.c.) measurements were performed on a Varian apparatus fitted with five TSK columns calibrated with polystyrene standards. Glass transition temperatures of linear and cyclic polymers were measured on a Mettler differential scanning calorimetry apparatus in the second heating cycle.

## SYNTHESIS AND CHARACTERIZATION OF CYCLIC POLYMERS

### *Cyclic poly(vinyl ether)s*

The direct synthesis of cyclic poly(vinyl ether)s from α,ω-heterodifunctional precursors has recently been described[19,21]. The strategy developed is illustrated in the case of poly(chloroethyl vinyl ether)s in *Scheme 4*. In a preliminary step, an α,ω-heterodifunctional poly(CEVE) **3** with α-styrenyl and ω-acetal ends is synthesized as a linear precursor. It is prepared by the selective initiation of the living cationic polymerization of CEVE at the α-iodo ether function of initiator **2**, which bears a styrenyl group. At low temperature (below −30°C) and in a low polarity solvent, the propagation reaction catalysed by zinc halides proceeds without any detectable reaction of the styrenyl unsaturation of the initiator, as demonstrated by the $^{1}H$ n.m.r. spectra and g.p.c. chromatograms of poly(CEVE)s presented in *Figures 2* and *3*, respectively. α,ω-Heterodifunctional poly(CEVE)s of $\bar{M}_n$ up to 20 000 and with narrow MWD (<1.2) have been prepared according to this procedure. It is worth noting that the macromonomer structure of the polymers makes them useful for the preparation of tailor-made macromolecular architectures.

Chain cyclization by end-to-end coupling was performed in a completely separate stage. To operate at high dilution, the solution of linear living poly(CEVE) was added dropwise to a large volume of toluene containing the strong Lewis acid $SnCl_4$ as reaction catalyst. The latter facilitates the fast reaction of ω-iodo ether termini with α-styrenyl polymer head-groups. Finally, the reaction medium was neutralized with a mixture of methanol and ammonia.

The quantitative reaction between the two polymer end-groups is demonstrated by the complete absence from the poly(CEVE) $^{1}H$ n.m.r. spectra of peaks for styrenyl unsaturations and acetal termini, the latter of which should have been formed by deactivation of the polymer with methanol (see *Figure 2*).

The cyclic structure of the poly(CEVE)s is further confirmed by the reduction in hydrodynamic volume for the cyclized polymer, as shown by the increase in the g.p.c. elution volume ($M_{pcycl}/M_{plin} \approx 0.85$), and the higher glass transition temperature. Some characteristics of linear and cyclic poly(CEVE)s are given in *Table 1*. It

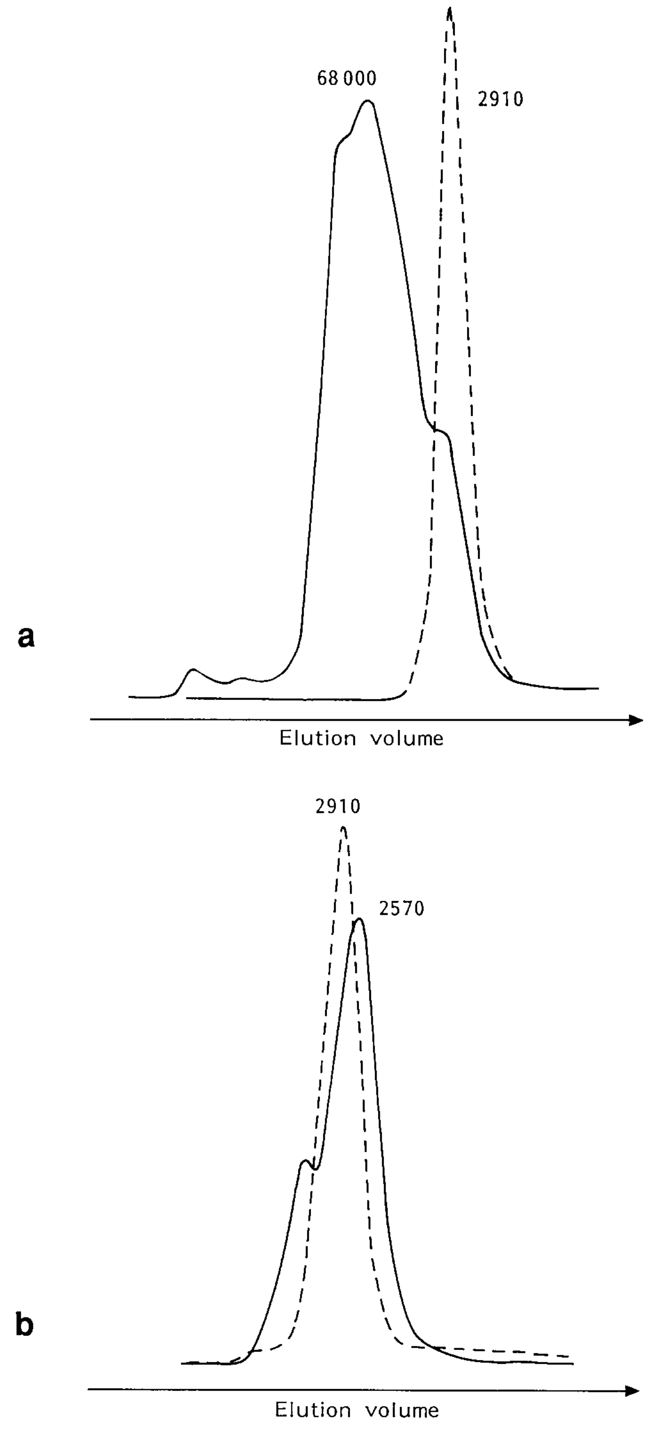


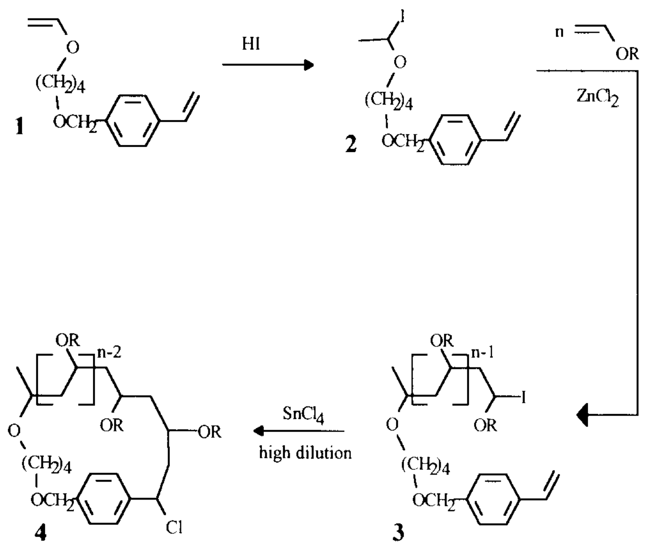
**Figure 3** S.e.c. curves of poly(CEVE)s (initial $\overline{DP}_n=25$) obtained before (---) and after (——) reaction with $SnCl_4$ and apparent peak molecular weights (polystyrene calibration): (a) in a concentrated toluene solution ($10^{-2}$ M); (b) in high dilution conditions

can be seen that the polydispersities of the cyclized polymers remain narrow (~1.2) and the fractions of polycondensates of higher molecular weights are quite low, in agreement with a relatively clean cyclization process.

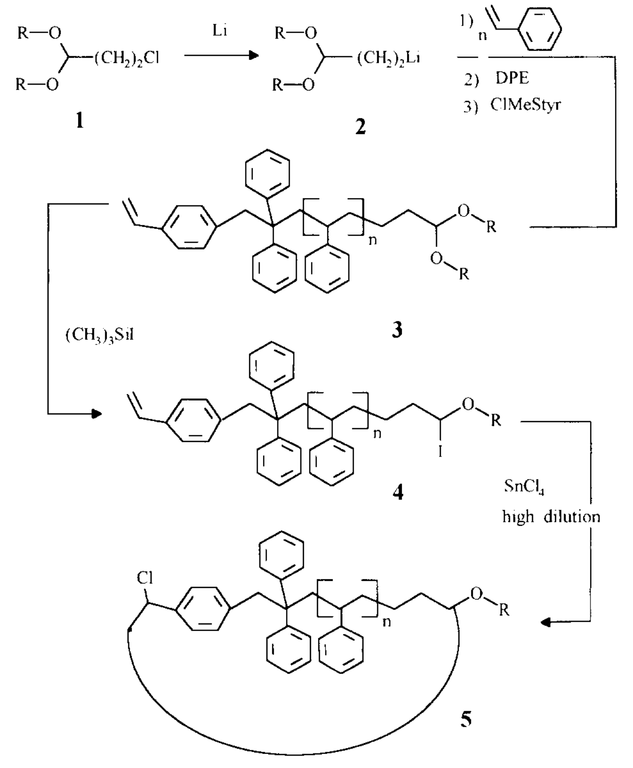
### *Cyclic polystyrenes*

The synthesis of macrocyclic polystyrenes by end-to-end coupling of dicarbanionic linear precursors in the presence of a difunctional nucleophile, as shown in *Scheme 2*, and the specific properties induced by the ring architecture have been investigated in detail by several groups. In spite of some discrepancies between the reported data, they can be used as valuable references to check the present cyclization procedure.

In order to obtain macrocyclic polystyrenes by direct unimolecular coupling, the first step of the synthetic pathway used for vinyl ethers (*Scheme 4*) was adapted to the preparation of a linear $\alpha,\omega$-heterodifunctional polystyrene by anionic polymerization[20]. The procedure (method I) is presented in *Scheme 5*. To introduce an acetal end-group, the living anionic polymerization of styrene was initiated by lithiopropionaldehyde diethylacetal **2** prepared from **1**. After the polymerization was complete,



**Scheme 4** Synthesis of a macrocyclic poly(chloroethyl vinyl ether). $R=CH_2CH_2Cl$



**Scheme 5** Strategy for the synthesis of macrocyclic polystyrenes (method I)

the styrenyl end-group was incorporated by reacting the living polystyrene successively with diphenylethylene (DPE) and *p*-chloromethylstyrene. The $^1$H n.m.r. spectrum of an $\alpha,\omega$-heterodifunctional polystyrene **3** is shown in *Figure 4*. It can be seen that the ratio between acetal and styrenyl groups is 1:1. The good agreement between theoretical and experimental polymer $\overline{DP}_n$ values, calculated either from n.m.r. spectra assuming one acetal and one styrenyl group per chain or from g.p.c. molecular weights, also confirms the polymer structure. Some characteristics of the heterodifunctional poly(styrene)s are collected in *Table 2*.

It has been shown elsewhere[22] that trimethylsilyl iodide reacts with acetals, which are quantitatively converted into $\alpha$-iodo ethers. The acetal end-groups of the polystyrene precursors were thus reacted with trimethylsilyl iodide in slight excess in order to generate heterodifunctional polystyrenes with $\alpha$-iodo ether and styrenyl termini **4**, as in the case of poly(vinyl ether).

The polystyrene ring closure was finally achieved, as indicated with poly(CEVE), by the slow addition of the heterodifunctional polystyrene precursor solution to a large volume of toluene containing a small amount of $SnCl_4$ as reaction catalyst. However, as indicated by the ratio $\langle G\rangle = M_{\mathrm{pcycl}}/M_{\mathrm{plin}}$ (*Table 2*), the cyclization yields were lower than expected, and reproducibility in the same set of experiments was not good. These results were attributed to the relatively poor stability of the $\alpha$-iodo ether end-groups of the polystyrene precursors.

A simplified and more efficient procedure (method II) has recently been developed to overcome this problem. It consists of the direct addition of the acetal-terminated polystyrene precursor **3** to a large volume of $CH_2Cl_2$ containing $SnCl_4$ and traces of water (*Scheme 6*). In these conditions the acetal terminus is directly converted into an active group, probably a carbocation, which

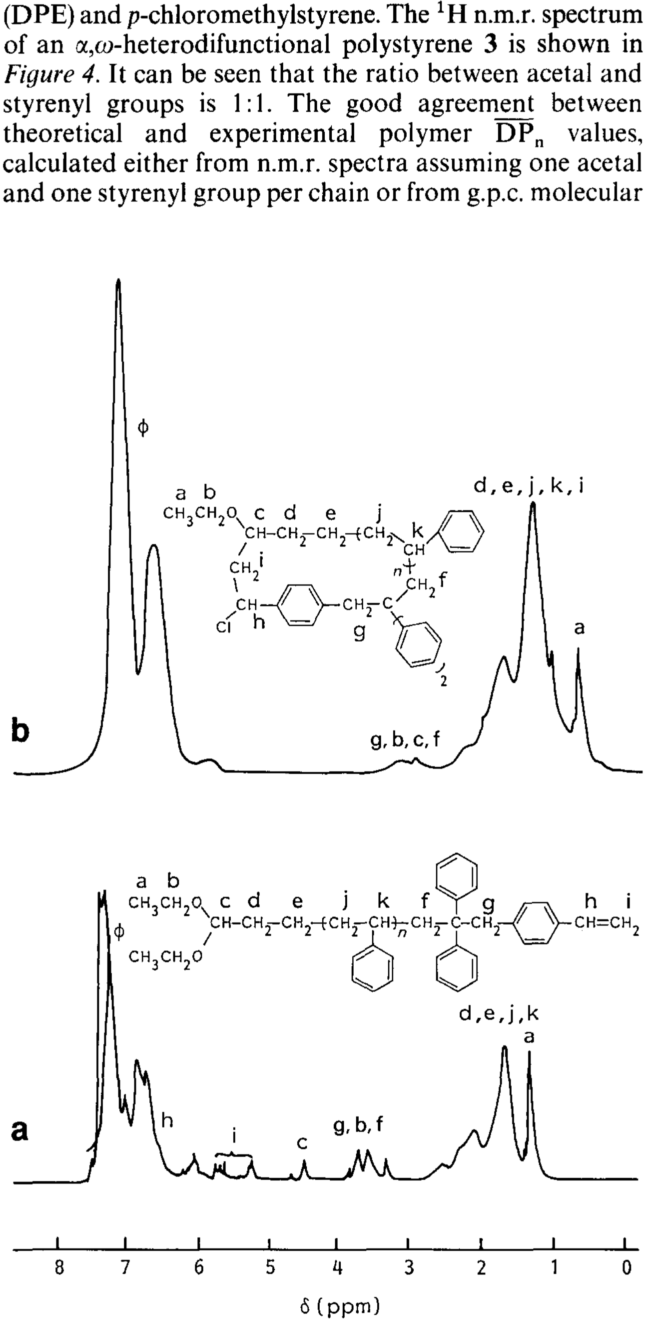
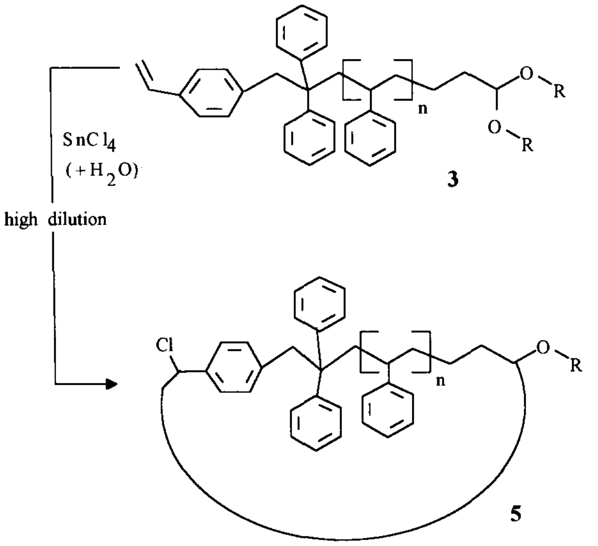


**Figure 4** $^1$H n.m.r. spectra of (a) an $\alpha$-styrenyl-$\omega$-acetalpolystyrene ($\overline{DP}_n = 20$) and (b) the corresponding cyclized polystyrene obtained according to method II



**Scheme 6** Direct cyclization by activation of an acetal end-group (method II)

**Table 1** Characteristics of linear and cyclic poly(CEVE)s obtained according to *Scheme 3*

| $\overline{DP}_n$ (theoretical) | Chain architecture | $M_p$[a] | $\bar{M}_n$[b] | $\bar{M}_w/\bar{M}_n$ | $\langle G\rangle$[c] | $T_g$[d] (°C) |
|---|---|---|---|---|---|---|
| 8 | Linear | 990 | 1140 | 1.08 | | −48 |
| | Cyclic | 846 | 850 | 1.26 | 0.85 | −32 |
| 20 | Linear | 2570 | 2320 | 1.16 | | −27 |
| | Cyclic | 2230 | 2150 | 1.30 | 0.87 | −14 |
| 25 | Linear | 2910 | 2860 | 1.19 | | −20 |
| | Cyclic | 2570 | 2660 | 1.23 | 0.87 | −12 |

[a] Apparent peak molecular weight determined by gel permeation chromatography using linear polystyrene standards
[b] Determined by gel permeation chromatography
[c] $\langle G\rangle = M_{\mathrm{pcycl}}/M_{\mathrm{plin}}$
[d] Determined for fractionated samples

**Table 2** Characteristics of linear α,ω-heterodifunctional polystyrenes and the corresponding cyclic polystyrenes obtained by direct coupling

| Method of preparation[a] | Chain architecture | $M_p$[b] | $\bar{M}_n$[c] | $\bar{M}_w/\bar{M}_n$ | $\langle G \rangle$[d] | $T_g$ (°C) |
|---|---|---|---|---|---|---|
| I | Linear | 1870 | 1780 | 1.03 | | 58 |
| | Cyclic | 1670 | 1640 | 1.04 | 0.85 | 78 |
| I | Linear | 3860 | 3720 | 1.05 | | 66 |
| | Cyclic | 3120 | 3200 | 1.06 | 0.82 | 83 |
| II | Linear | 1780 | 1700 | 1.04 | | 60 |
| | Cyclic | 1420 | 1450 | 1.05 | 0.80 | 77 |
| II | Linear | 3860 | 3720 | 1.04 | | 73 |
| | Cyclic | 3100 | 3200 | 1.08 | 0.78 | 96 |
| II | Linear | 12 600 | 12 200 | 1.04 | | 91.5 |
| | Cyclic | 9800 | 9880 | 1.05 | 0.78 | 101 |

[a] For method I see *Scheme 5* and for method II see *Scheme 6*

[b] Apparent peak molecular weight determined by gel permeation chromatography using linear polystyrene standards

[c] Determined by gel permeation chromatography

[d] $\langle G \rangle = M_{\mathrm{pcycl}}/M_{\mathrm{plin}}$

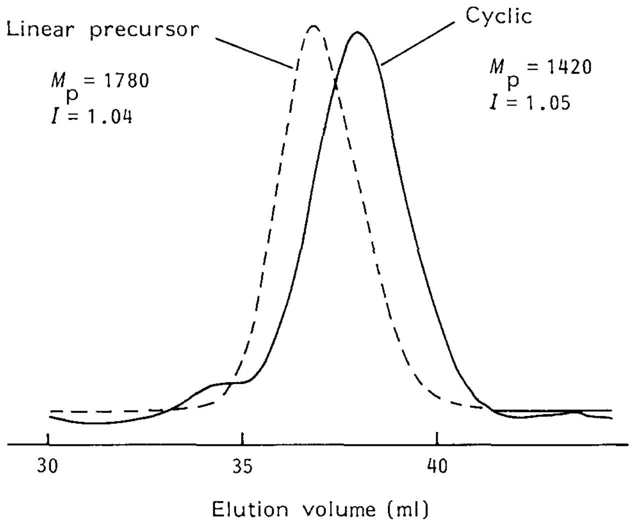
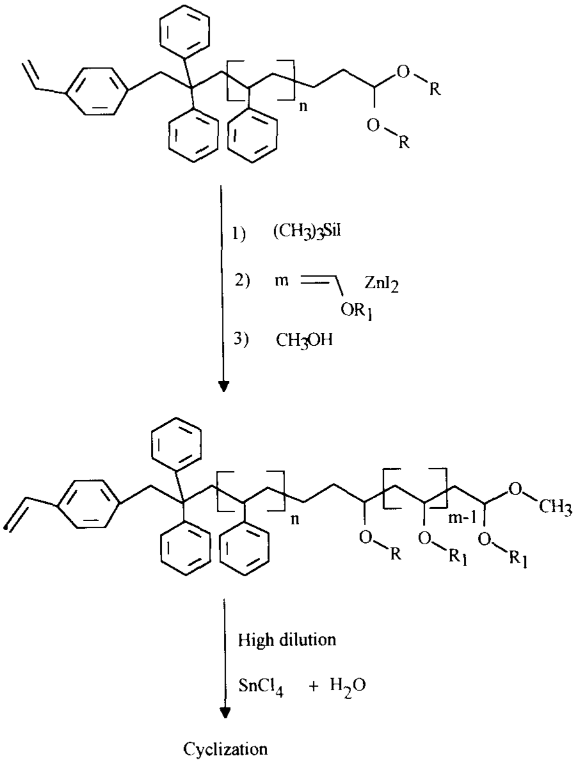


**Figure 5** G.p.c. curves of linear α-styrenyl-ω-acetalpolystyrene (initial $\overline{DP}_n = 16$) and the corresponding cyclized polystyrene prepared according to method II. Analyses were performed on the crude cyclized reaction products without any fractionation procedure ($I$ = MWD)



**Scheme 7** Synthesis of a macrocyclic poly(styrene-*b*-chloroethyl vinyl ether) copolymer. $R = CH_3-CH_2$, $R_1 = CH_2-CH_2Cl$

immediately reacts with the styrenyl unsaturation to form the cyclic polymer in good yield. The characteristics of some linear and cyclic polystyrenes can be compared in *Table 2*. Typical g.p.c. chromatograms for a linear polymer and the corresponding cyclic polymer, without any fractionation procedure, are shown in *Figure 5*. It can be seen that only a very small amount of polycondensate is formed and the main g.p.c. peak, corresponding to cyclics, remains extremely narrow (MWD < 1.1). This shows that cyclic polystyrenes of high purity can be prepared according to this procedure. Besides the use of well-defined α,ω-heterodifunctional precursors with stable end-groups, the possibility of operating at extremely low concentrations and at stoichiometry between the reactive functions is a likely determining factor for the high cyclization yields obtained.

### *Cyclic poly(styrene-*b*-CEVE) copolymers*

Application of this cyclization pathway to the synthesis of diblock copolymers has recently been investigated[23]. The procedure used for the preparation of the α,ω-heterodifunctional diblock precursor is described in *Scheme 7*. It involves in a first step the synthesis of an α,ω-heterodifunctional polystyrene as already described, from which the growth of a poly(CEVE) block is initiated. The initiation is performed by the quantitative transformation with TMSI of polystyrene α-acetal end-groups into α-iodo ether functions. CEVE polymerization is then started by adding the monomer and a catalytic amount of $ZnCl_2$. After the conversion is complete the chains are deactivated by adding a mixture of methanol and ammonia, thus leading to α,ω-heterodifunctional diblock copolymers. The cyclization step is then identical to the one applied for polystyrene. Typical g.p.c. chromatograms of the linear polystyrene precursor, the linear poly(styrene-*b*-CEVE) diblock and

**Table 3** Characteristics of linear α,ω-heterodifunctional poly(styrene-*b*-CEVE)s and the corresponding cyclic poly(styrene-*b*-CEVE)s obtained by direct coupling (see *Scheme 7*)

| Chain architecture | $\overline{DP}_n$[a] (n.m.r.) | $\bar{M}_n$ (theoretical) | $M_p$[b] | $\bar{M}_w/\bar{M}_n$ | $\langle G \rangle$[c] | $T_g$ of blocks (°C) Polystyrene | Poly(CEVE) |
|---|---|---|---|---|---|---|---|
| Linear polystyrene[d] | 18 | 1800 | 2200 | 1.07 | | 66 | |
| Linear poly(styrene-*b*-CEVE) | 18 and 20 | 4416 | 4350 | 1.08 | | 47 | −1.3 |
| Cyclic poly(styrene-*b*-CEVE) | 18 and 20 | 4420 | 3520 | 1.16 | 0.81 | 85 | 25 |
| Linear polystyrene[d] | 23 | 2820 | 2515 | 1.02 | | 68 | |
| Linear poly(styrene-*b*-CEVE) | 23 and 33 | 7390 | 6400 | 1.15 | | 70 | −0.8 |
| Cyclic poly(styrene-*b*-CEVE) | 23 and 33 | 7384 | 5200 | 1.24 | 0.81 | 88 | 0.6 |

[a] Determined on the basis of end-groups

[b] Apparent peak molecular weight determined by gel permeation chromatography using linear polystyrene standards

[c] $\langle G \rangle = M_{\mathrm{pcycl}}/M_{\mathrm{plin}}$

[d] α,ω-Heterodifunctional polystyrene used as chain initiator

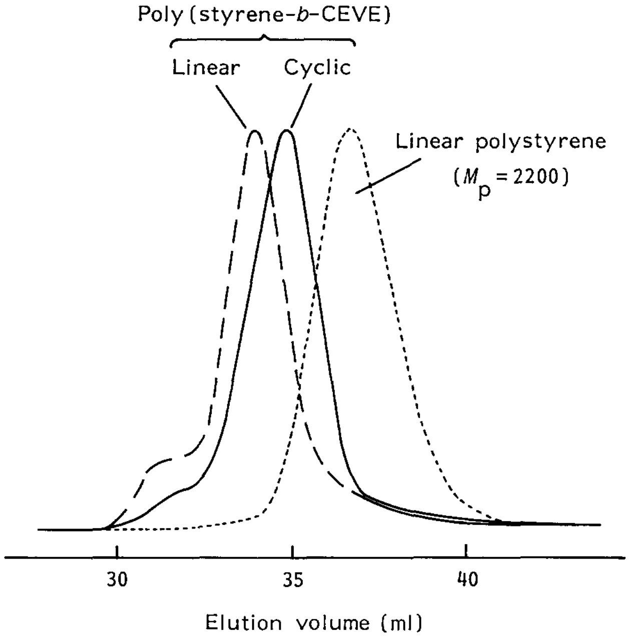


**Figure 6** G.p.c. curves of a linear α-styrenyl-ω-acetalpolystyrene ($\overline{DP}_n$ = 18), a linear α-styrenyl-ω-acetalpoly(styrene-*b*-CEVE) and the corresponding cyclic diblock copolymer. Analyses were performed on the crude reaction products without any fractionation procedure

the corresponding cyclic diblock are presented in *Figure 6*. Some characteristics of the copolymers are summarized in *Table 3*. Again, the cyclic structure of the final copolymers may be deduced from the absence from the n.m.r. spectra of peaks for the terminal functions of the chains, the shift in the g.p.c. signals towards apparent lower molecular weights ($\langle G \rangle = 0.8$) and the increase in the glass transition temperature of the two blocks.

Further work concerning a more detailed investigation of the properties of these cyclic polymers and copolymers and the application of this technique to the preparation of other macromolecules characterized by a macrocyclic architecture and a controlled size is in progress and will be reported in forthcoming papers.

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