A New Strategy for the Synthesis of Cyclic Polystyrenes: Principle and Application

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ABSTRACT: A new strategy for the synthesis of vinyl type macrocyclic polymers of controlled molecular weight and molecular weight distribution has been investigated. It involves the direct coupling of an α,ω-heterodifunctional linear polymer precursor previously prepared by living polymerization. The cyclization is achieved under high dilution, by appropriate activation of one of the polymer ends in order to allow its reaction with the other end function. The theoretical advantages of this approach compared to the conventional procedure involving the coupling of a living homodifunctional polymer precursor by a difunctional organic molecule are discussed. This new technique has been applied to the synthesis of cyclic polystyrenes with high yields (≥85–90%). The structural characterization of the polymers as well as some of their thermal properties is also reported.

Introduction

The synthesis, the structural characterization, and a detailed investigation of the properties of cyclic polystyrenes have concentrated important research efforts in the last 10 years. Most of the strategies developed[1-6] to cyclize polystyrene chains involve the end-to-end ring closure of a living α,ω-dicarbanionic polystyrene by coupling the two active ends with a difunctional nucleophile (dibromo-*p*-xylene,[1] dimethyldichlorosilane,[2] etc.), under highly diluted conditions.

As illustrated in Scheme 1, the cyclization procedure may be viewed as a two-stage reaction. It involves in the first step (a) a bimolecular condensation between the two difunctional species, i.e. the linear polymer and the organic compound, leading to an α,ω-heterodifunctional polystyrene intermediate. This short-lived species then reacts in a second stage by an intramolecular process (b), unimolecular in nature, involving its two hetero ends, to finally lead to the cyclized polymer.

It is clear that in the very dilute conditions used, both the number of coreactants involved, their purity (stability of active centers), and the presence of several stages in the cyclization process have a crucial effect on the yield in cyclic compounds. The bimolecular coupling reaction which constitutes the first stage of the process is in particular highly disfavored at the very low concentrations used (typically $<10^{-5}$ M). Moreover, to limit the possibility of successive intermolecular couplings which result in undesirable polycondensates, it is essential to perform the whole reaction process while the stoichiometry between the two reactive functions is kept constant. These points have been discussed recently in detail by Hogen-Esch.[7]

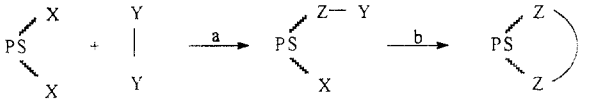
Owing to these considerations, a new strategy for the synthesis of macrocyclic polystyrenes and, more generally, of macrocyclic polymers was investigated. The approach developed consists of a single step, pseudo-unimolecular, cyclization process.

The principle of the synthesis as well as the first results obtained in the case of polystyrene chains are presented in this paper.

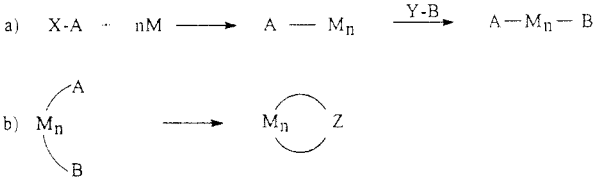
Strategy of the Synthesis

The general scheme followed for the synthesis of macrocyclic polymers is presented in Scheme 2. It involves two completely separated steps.

Scheme 1. Conventional Bimolecular Cyclization Procedure



Scheme 2. Unimolecular Cyclization of an α,ω-Heterodifunctional Precursor



(a) Synthesis of an α,ω-Heterodifunctional Linear Precursor (A-M_n-B). Linear α,ω-heterofunctionalized polymers can be prepared by means of living polymerization. The procedure involves initiation of the polymerization with a functional initiator (X-A), in order to introduce a first function in the α-position, and deactivation of the living polymerization by a functionalized terminating agent (Y-B). The latter allows one to place a different end function group in the ω-position.

In the described procedure, moreover, the A and B functions must be able to couple directly after their appropriate activation or modification.

(b) Cyclization of A-M_n-B into $\overset{\frown}{M_n Z}$. Intramolecular end-to-end cyclization of the linear α-A,ω-B-heterodifunctional polymer is performed in a totally separated stage. It involves the direct coupling of the two end functions, or of their derivated forms, under very high dilution. Under these conditions, the unimolecular one-step cyclization should be highly favored compared to bimolecular interchain processes, leading to polycondensates. Furthermore, owing to an expected good bifunctionality of the linear precursors, a constant stoichiometry between reactive antagonist ends can be respected all along the cyclization process.

A similar strategy has been used for the synthesis of cyclic poly(chloroethyl vinyl ether)s.[8] It is now applied to the preparation of cyclic polystyrene oligomers of controlled dimensions.

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Experimental Section

(1) Preparation of 3-Lithiopropionaldehyde Diethyl Acetal (2). Lithium powder (0.0168 mol) was introduced under nitrogen in a compartment of a double chamber glass apparatus equipped with a central fritted filter and two PTFE stopcocks and slurried into freshly distilled and dried diethyl ether (20 mL). After cooling at −30 °C, 3-chloropropionaldehyde diethyl acetal (Aldrich, 1.4 g, 8.4×10^{-3} mol), previously dried over calcium hydride, was added to the slurry. The mixture was then stirred for 18 h at −30 °C, and the solution was transferred by filtration into the second compartment of the apparatus and kept at −30 °C until use.

(2) Preparation of the Model Compound. 3-Lithiopropionaldehyde diethyl acetal (8.4×10^{-3} mol in 20 mL of diethyl ether) was transferred under dry nitrogen into a glass flask and reacted at room temperature for about 1 h successively with 1,1-diphenylethylene (1.1 equiv with respect to the initiator) and *p*-(chloromethyl)styrene (1.2 equiv with respect to the initiator). The resulting solution was washed several times with water and filtered, and the crude product was recovered by solvent evaporation. The model compound was finally purified by preparative GPC before its characterization.

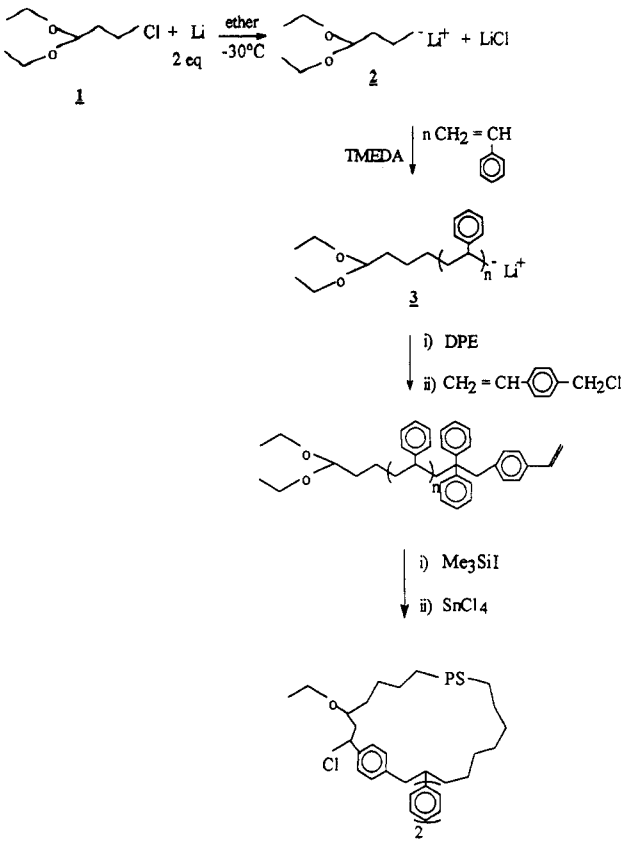
(3) Polymerization. The living anionic polymerization of styrene was carried out in benzene at room temperature. Freshly dried solvent (70 mL), styrene (2.4×10^{-2} to 5.8×10^{-2} mol), and *N,N,N′,N′*-tetramethylethylenediamine (1.1 equiv with respect to the initiator) were successively introduced into the polymerization reactor under dry nitrogen. 3-Lithiopropionaldehyde diethyl acetal (2) was then added to the solution to initiate the polymerization. A rapid red coloration of the solution was observed. After 1–3 h, the living polymer was reacted with 1,1-diphenylethylene (1.1 equiv with respect to the initiator), leading to a darker red solution. Finally, after about 15 min, dried *p*-(chloromethyl)styrene (1.2 equiv with respect to the initiator) was added to the solution, leading immediately to transformation of polystyrene ends, as shown by the rapid change of the medium to colorless, or slightly yellow. The resulting polymer was recovered by partial solvent evaporation and precipitation into methanol and dried under vacuum.

(4) Cyclization. The heterodifunctional polystyrene (0.2–1 g) was dissolved under dry nitrogen in freshly distilled and dried toluene (100 mL) and placed in a dropping funnel refrigerated at −50 °C. Then it was reacted with trimethylsilyl iodide (TMSI) (acetal ends/TMSI = 1:1.5, 1.6×10^{-4} mol) for 30 min. The polymer solution was then added dropwise (in 5–6 h), under nitrogen, to a large volume of dry toluene (1500 mL) containing 1.9×10^{-4} mol of $SnCl_4$ and thermostated at −10 °C. The mixture was allowed to stand an additional 30 min, and a solution of ammonia and methanol was introduced to neutralize the system. The polymer solution was finally filtered and washed and the crude cyclized polymer recovered by solvent evaporation under vacuum and, when possible, by precipitation into methanol.

For studies concerning the effect on cyclization yields of temperature, reaction time, and active end concentration, experiments were performed in a Schlenk apparatus. The solvent, the linear polymer precursor, and TMSI were first introduced and reacted under a dry atmosphere for 20 min. Then a small amount of $SnCl_4$ (2 equiv with respect to the α-iodo ether ends) was added to the solution, and the mixture was allowed to react under fast stirring for a given time. The reaction was stopped by adding methanol and ammonia and the solution was washed several times with water, dried over $MgSO_4$, and analyzed by GPC.

(5) Polymer Characterization. Proton NMR spectra were recorded in $CDCl_3$ on a Bruker AC 250 FT apparatus. GPC measurements were performed in THF on a Varian apparatus equipped with refractive index/UV dual detection and fitted with three TSK columns (G2000 HXL, G3000 HXL, G4000 HXL) calibrated with polystyrene standards. A trace of toluene, added to the sample, was used as the internal flow marker reference. Glass transition temperatures of the polymers were measured on a DSC Perkin-Elmer apparatus at the second heating cycle and at a heating rate of 10 °C/min.

Scheme 3. General Reaction Pathway for the Synthesis of Cyclic Polystyrenes



Results and Discussion

The detailed synthetic approach used for the synthesis of cyclic polystyrenes is described in Scheme 3.

(1). Synthesis of an α,ω-Heterodifunctional Polystyrene. Linear α-diethyl acetal, ω-styrenyl polystyrenes of controlled $\overline{DP}_n$, used as cyclizing precursors, were synthesized by living anionic polymerization according to the following process:

(a) The α-diethyl acetal head group was introduced from initiation of the styrene polymerization with 3-lithiopropionaldehyde diethyl acetal[9] (2). The latter was obtained from reaction of 3-chloropropionaldehyde diethyl acetal (1), in the presence of a slight excess of lithium, Scheme 3. Anionic polymerizations were performed in benzene in the presence of a small amount of TMEDA as additive, to allow a better control of the initiation step.[9] As may be seen in Table 1, a good agreement between experimental and theoretical $\bar{M}_n$, as well as narrow molecular weight distributions (MWD) ($I < 1.1$) were observed in these conditions, indicating that polymerization initiated by 3-lithiopropionaldehyde diethyl acetal proceeds cleanly without any detectable side reactions.

(b) The ω-styrenyl end group was introduced, after the polymerization was complete, by reacting the living polystyryllithium 3 successively with diphenylethylene (DPE) and *p*-(chloromethyl)styrene (P-ClMS), Scheme 3. The addition of DPE onto the polystyryl ends was essential to suppress the reaction of the carbanion onto the styrenyl unsaturation of P-ClMS and selectively orient the reaction in the direction of chloride substitution. This was confirmed by analysis of the polymer end groups by proton NMR.

In order to make a precise assignment of signals of polystyrene end groups, a model compound was first synthesized according to the same synthetic pathway used for the polymerization; see Scheme 4. The proton NMR

Table 1. Characteristics of Linear α-Acetal, ω-Styrenyl Heterodifunctional Polystyrenes (Polymerization Conditions: Room Temperature, Reaction Time, 1-3 h; Solvent, Benzene)

[styrene], 10^{-1} M	[acetal][a], 10^{-1} M	$\overline{DP}_n$(th)	$\overline{DP}_n$(exp)[b]	$\overline{DP}_n$(exp)[c]	$\bar{M}_n$(th)	$\bar{M}_n$(exp)[b]	$\bar{M}_w/\bar{M}_n$	styrenyl ends/acetal ends[d]
2.4	0.16	15	14		2000	1900	1.04	
2.4	0.14	17	15.1	18.5	2200	2060	1.05	0.97
3	0.15	20	19	23.5	2500	2400	1.04	1.08
9.6	0.32	30	27	28.6	3500	3200	1.07	
5.8	0.097	60	57.4	59.6	6650	6400	1.03	0.97

[a] 3-Lithiopropionaldehyde diethyl acetal. [b] Determined by GPC. [c] Determined by ^{1}H NMR. [d] Determined by ^{1}H NMR from the ratio of protons: $=CH_2/HC$

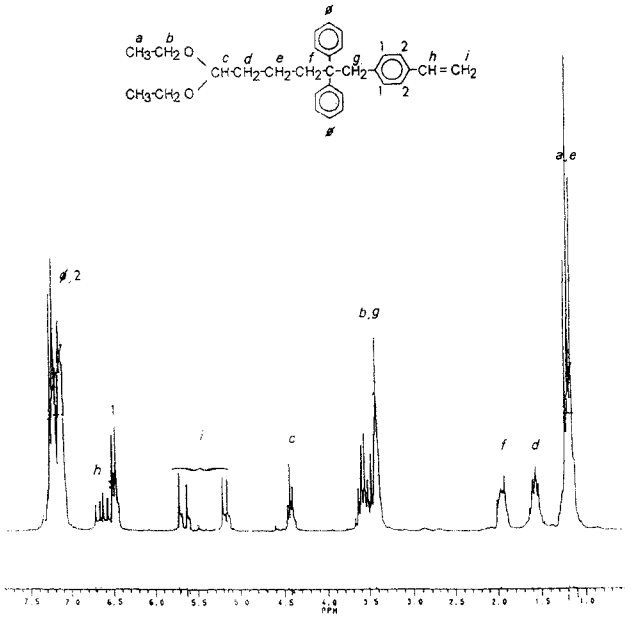


Figure 1. ^{1}H 250 MHz NMR spectrum of a model compound of polymer ends. Solvent: $CDCl_3$.

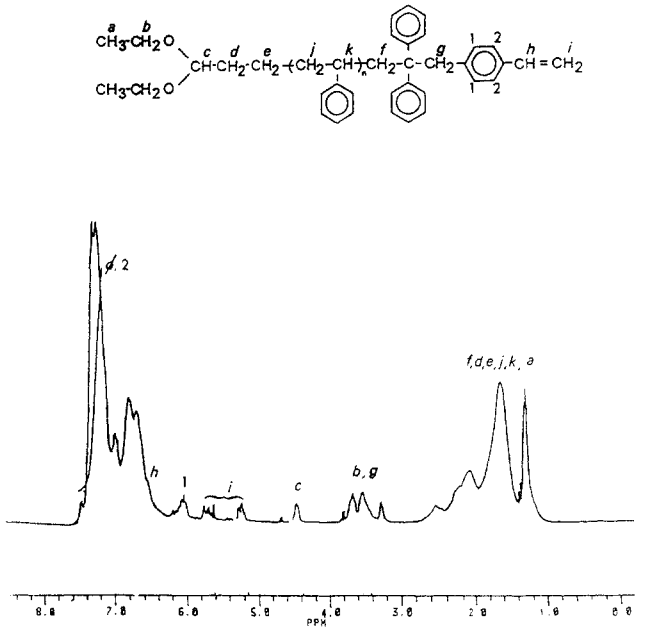
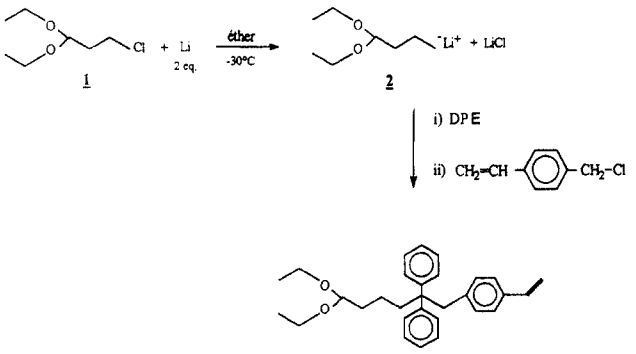


Figure 2. ^{1}H NMR spectrum of a linear α-acetal, ω-styrenyl polystyrene of $\bar{M}_n$ = 2060. Solvent: $CDCl_3$.

Scheme 4. Synthesis of a Model of the Linear α-Acetal, ω-Styrenyl Polystyrene Precursor



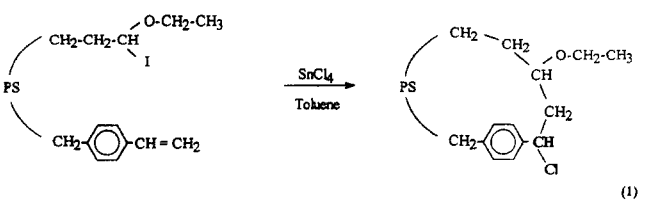
spectra and the peak assignment of the model compound and of an α-diethyl acetal, ω-styrenyl polystyrene ($\overline{DP}_n$ = 17) are shown in Figures 1 and 2, respectively.

The relative numbers of α-acetal and ω-styrenyl end groups per chain were determined from the area of peaks of the acetal proton (c) and the methyls (a) of the acetal group on the one hand and of the methylene (i) of the styrenyl unsaturation on the other hand. As can be seen, the ratio between acetal and styrenyl groups is very close to 1. This was verified for all the low molecular weight polystyrenes prepared; see Table 1.

2. Cyclization. The procedure applied to directly couple the two antagonist functional polystyrene ends of the same chain is derived from the one described in a previous paper[8] for the cyclization of α,ω-heterodifunctional poly(chloroethyl vinyl ether)s.

In a first step, the α-acetal ends of the heterodifunctional polystyrenes were quantitatively transformed into α-iodo ether termini, by reacting, in relatively concentrated conditions ([acetal ends] = 10^{-3} M), the polystyrene with trimethylsilyl iodide[10] in slight excess (1:1.5), as indicated in Scheme 5.

The chain cyclization, by end-to-end ring closure, was performed in a completely separate stage. A solution of the linear polystyrene, bearing an α-iodo ether functionality, was added dropwise to a large volume of toluene containing a strong Lewis acid, $SnCl_4$, in a catalytic amount. The latter strongly activates (likely ionizes) the α-iodo ether ends which then react with the ω-styrenyl polymer end groups, leading to an inactive or weekly active chloro adduct, likely according to the reaction schematized in eq 1.



(1)

Finally, the reacting medium was neutralized by adding a solution of methanol and ammonia.

This procedure allows the reaction to proceed under extreme dilution of active species, and at a constant stoichiometry between reactive functions, conditions which should highly favor intramolecular (cyclization) over intermolecular reactions (polycondensation).

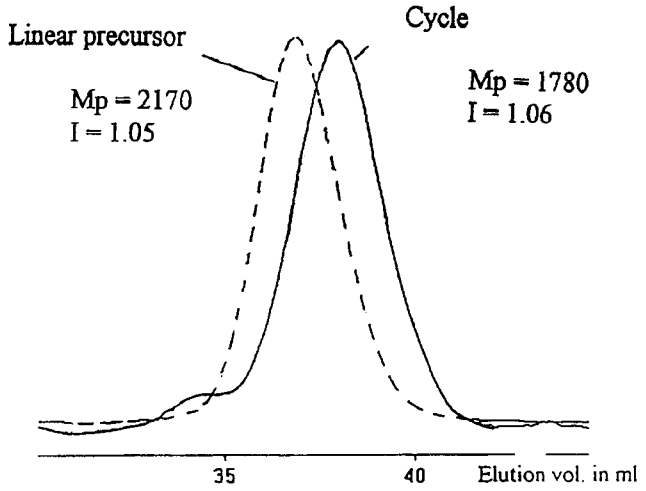
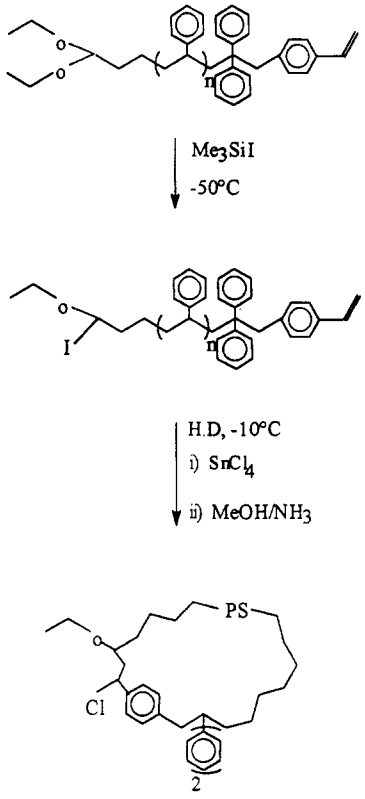


Figure 3. GPC curves of linear α-acetal, ω-styrenyl polystyrene of $\bar{M}_n$ = 2060 obtained before and after the cyclization process.

Scheme 5. Unimolecular Cyclization Step of an α,ω-Heterodifunctional Polystyrene Precursor



Experimental results supporting this view are now examined.

GPC Analysis. The GPC curves of an α-diethyl acetal, ω-styrenyl polystyrene and of the corresponding polymer recovered after reaction with $SnCl_4$ under high dilution, are presented in Figure 3. As may be seen, the polymer submitted to the cyclization process exhibits a main peak located at an elution volume higher than (lower molar masses) the linear one. This is what we could expect and what is generally observed for cyclic and linear macromolecules of the same $\overline{DP}_n$,[11] due to the lower hydrodynamic volume of cyclic polymers. The small peak observed at the lower elution volume also indicates the presence, but a very small proportion, of polymers of higher molecular weights. Their formation may be attributed to intermolecular chain coupling. Yields of "cyclized" polystyrene, calculated on the basis of the relative area of peaks attributed to cyclic polystyrenes and of crude products (cyclics + polycondensates), are reported in Table 2. In most cases, they reach 80–85%.

Table 2. Characteristics of Linear α,ω-Heterodifunctional Polystyrenes and of the Corresponding Cyclic Polystyrenes[a]

$\overline{DP}_n$	archit	M_p,[b]	$\bar{M}_n$[c]	I	$\langle G_{exp}\rangle$[d]	% of cycles[e]	T_g, °C[e]
	lin	2110	1900	1.04			58
14	cyc	1790	1740	1.05	0.85	80	78
	cyc	1750	1650	1.06	0.83	67	
15.1	lin	2170	2060	1.05			66
	cyc	1780	1810	1.06	0.82	85	83
27	lin	3350	3200	1.07			73
	cyc	2750	2600	1.08	0.82	85	95
57.4	lin	6670	6400	1.03			77
	cyc	5470	5250	1.04	0.82	85	99

[a] The latter were obtained by derivatization of the acetal end with Me_3SiI and reaction, under high dilution, with $SnCl_4$ in toluene. $T°$ reaction = −10 °C. [b] Apparent peak molecular weight determined by GPC using linear polystyrene standards. [c] Determined by GPC on the basis of polystyrene standards. [d] Ratio of the apparent molecular weights derived from GPC signals attributed to cyclics and linear precursors. [e] Measured on crude products.

The observed ratio of the apparent peak molecular weight (M_p) corresponding to the signal of cyclics—more exactly assumed to be cyclics—and linear polystyrene, denoted $\langle G_{exp}\rangle$ in order to differentiate it from the true $\langle G\rangle = M_{pc}/M_{pl}$, are in the range 0.85–0.82; see Table 2. These values are in good agreement with $\langle G_{exp}\rangle$ values reported in the literature[4] for macrocyclic polystyrenes. However, no dependence could be found between $\langle G_{exp}\rangle$ and the variation of polymer molecular weights, nor with changes in the ratio cyclics/polycondensates. Another hypothesis to explain the observed fluctuations of $\langle G_{exp}\rangle$ could be the presence of uncyclized linear precursors in admixture with cyclized chains. Owing to the partial overlapping of the GPC traces of linear and cyclized polymers (see Figure 3), the M_{pc} could be shifted to a lower elution volume by the presence of unreacted linear chains, and consequently, the corresponding $\langle G_{exp}\rangle$ value increased.

In order to test this assumption and determine the limits of GPC to detect the presence of uncyclized linear chains, increasing amounts of linear precursor were added to a fractionated cyclic sample and the mixtures were analyzed by GPC. The corresponding curves are shown in Figure 4. A slight peak broadening (I varies from 1.04 to 1.07) as well as a peak shift toward higher molar masses (G increases from 0.82 to 0.85) is clearly noticed already for the mixture containing 10% added linear polymer. These results support that cyclic samples obtained by this procedure are indeed low in linear content (<20%).

The cyclic structure and the characteristics of the polystyrenes were further investigated by several other analytical methods.

NMR Analysis. The ^1H NMR spectrum of a polystyrene submitted to cyclization is presented in Figure 5. It can be compared with that of its linear precursor given in Figure 2. The cyclized polystyrene spectrum is characterized by the almost complete disappearance of signals relative to the ω and α end groups, the styrenyl unsaturations (90–95%, according to $=CH_2$ peak intensity), and the α-iodo ethers or its acetal-derivatized forms,[12] respectively. These observations support an almost complete consumption of the two antagonist functions, very likely in the reaction process already described by eq 1. The resulting chloro adduct could not be however clearly identified on the NMR spectra.

Since on the basis of GPC traces we may consider that polycondensates (dimers + higher condensation products)

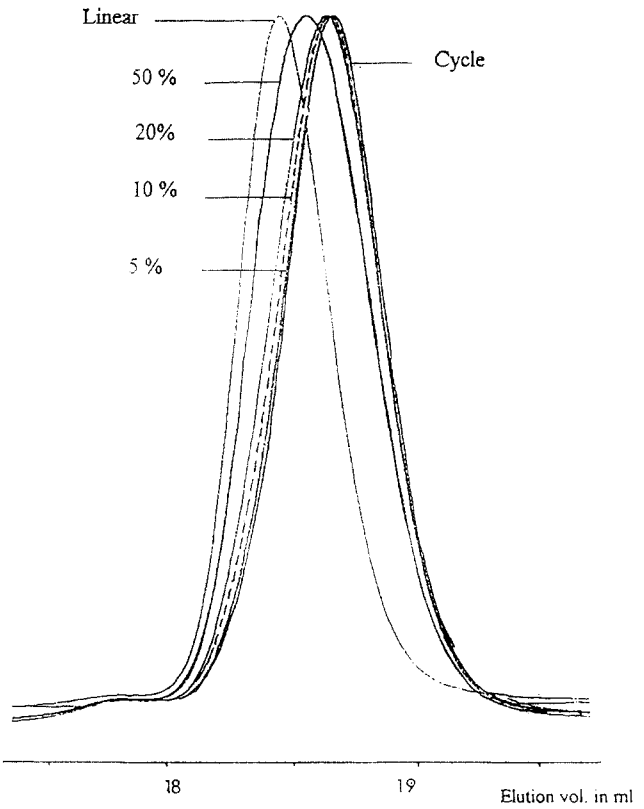


Figure 4. GPC curves of different mixtures of linear and macrocyclic polystyrenes of the same molecular weight ($\bar{M}_n$ = 2060).

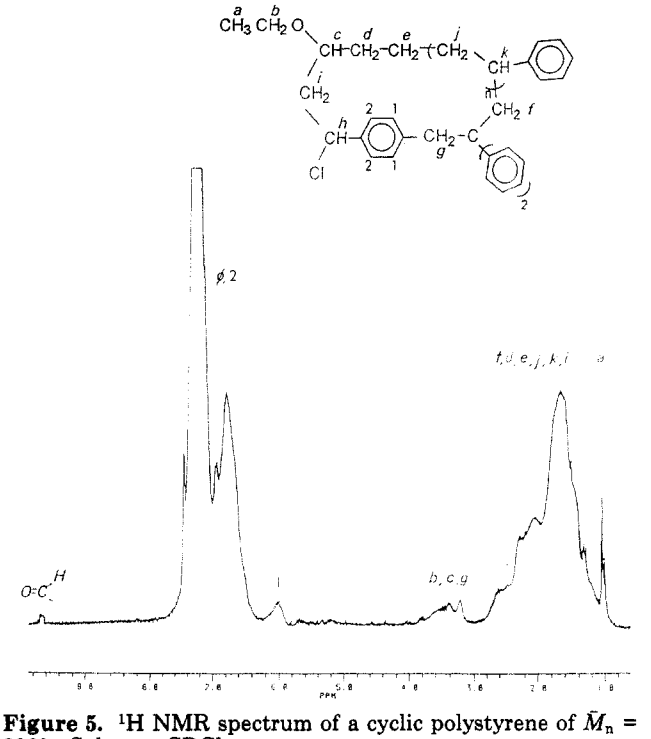


Figure 5. ^{1}H NMR spectrum of a cyclic polystyrene of $\bar{M}_n$ = 2060. Solvent: $CDCl_3$.

represent a very minor fraction (10–20% in most cases; see Table 2), these results imply that the reaction predominantly proceeds in an intramolecular fashion to lead to cyclic polymers.

Besides this main process, a small additional NMR signal, located at 9.7 ppm, and attributed to an aldehyde proton, indicates the side formation of aldehyde groups whose proportion however does not exceed ~10% of the total number of polystyrene chains. Their formation could

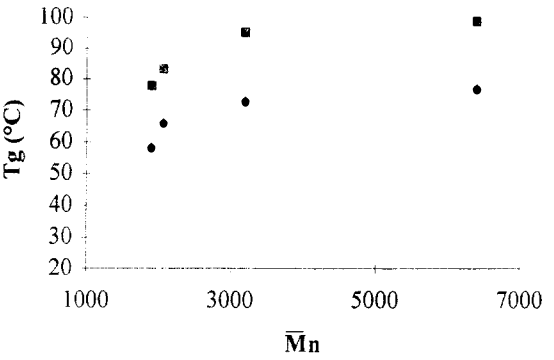


Figure 6. Variations of the glass transition temperatures of linear (◆) and cyclic (■) polystyrenes of increasing molecular weight.

result from a very partial de-activation of α-iodo ether ends during the cyclization process and explain the presence of some linear polystyrene contaminant (~10%), as already speculated.

DSC Analysis. The glass transition temperatures of linear and fractionated cyclic polystyrenes of various molar masses are given in Table 2. Their variation with increasing molecular weight is plotted in Figure 6. In agreement with a restriction of the mobility of the main chain, higher T_g's are observed for the cyclic derivatives; the difference between T_{gc} and T_{gl} is about 20 deg for the lower $\overline{DP}_n$'s. However, in contradiction with the literature data[1,2,4] which report an increase of T_{gc} with a decrease of $\overline{DP}_n$, a tendency of both T_{gc} and T_{gl} to decrease with $\overline{DP}_n$ is observed with the present cyclic polystyrenes. Though we cannot definitely rule out the effect of linear contaminants, their proportion (estimated to be less than 20%) makes this hypothesis unlikely. On the other hand, the great flexibility of the end-to-end linking unit constituted of the $-(CH_2)_3-CH(OEt)-CH_2-$ segment might drastically decrease T_{gc}, especially for very low $\overline{DP}_n$ cyclics, contrary to those used in other studies. Further work is necessary to test this possibility.

Though the above analytical results confirm the formation of polystyrene macrocycles as major reaction products, the presence of the remaining uncyclized precursor and of polycondensates leads us to examine the influence of reaction conditions on cyclization yields.

Effect of Temperature and Reaction Time. In order to determine the best conditions for cyclization, the influence of the temperature (T) and the time (t) of reaction was investigated. A series of cyclizations was performed by adding a given concentration of $SnCl_4$ ([α-iodo ether ends]:[$SnCl_4$] = 1:2) to a toluene solution of the α-iodo ether precursor ([C] = 7×10^{-4} M) maintained at a given temperature ranging from −50 to 0 °C. The crude polymer system was sampled at increasing reaction times, deactivated, and analyzed by GPC. The corresponding results are summarized in Table 3. The cyclization rate is faster at −10 °C than at −50 °C. At T = −10 °C, high yields in cyclic products are reached within 5 min, whereas it takes about 20 min at −50 °C. At final conversion, in the two cases the peak intensities correspond to about 80% of cyclics formed with respect to the total crude polymer.

At 0 °C, conversions of the precursor into cyclic products and polycondensates become extremely low, suggesting that active centers are very unstable in these conditions.

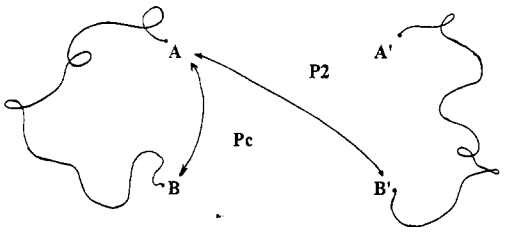
Effect of Active Ends Concentration on the Percentage of Cycles. To test the agreement between experimental results and theoretical values of chain

Table 3. Influence of Temperature (T) and Reaction Time (t) on the Percentage of Cycles Formed (Linear Precursor: $\bar{M}_n$ = 2060, [C*] = 7 × 10⁻⁴ M. solvent:toluene)

	−50 °C		−10 °C	
t, min	$\langle G_{exp}\rangle$[a]	% of cycles[b]	$\langle G_{exp}\rangle$[a]	% of cycles[b]
5	0.9		0.84	
20	0.84			
30	0.83		0.83	
60	0.82	82	0.82	
120	0.82	83	0.82	80

[a] Ratio of the apparent molecular weights derived from GPC signals attributed to cyclics and linear precursors. [b] Calculated from the GPC peak areas ratio, cyclics/crude product.

Scheme 6



cyclization predicted by Jacobson–Stockmayer type calculations,[13] we have investigated the influence of the active center's concentration and of the precursor chain length on the yields of cycles.[14] Optimized reaction conditions, described in section 2, were used (T = −10 °C, polymer precursor leading to $\langle G_{exp}\rangle$ = 0.82 and I cyclics = 1.05 under very dilute conditions).

This approach, already applied by Roovers[1] and Rempp[3] for the cyclization of α,ω-dicarbanionic polystyrenes with a difunctional nucleophile, considers that the probability for A and B ends of a chain to find each other (see Scheme 6) depends mainly on (1) the total concentration of macromolecules, assuming that there is neither preferential nor excluded volume for the chains, (2) the chain length, and (3) the mean square end-to-end distance of the polymer in solution.

P_c, the probability of intramolecular condensation leading to a cycle, may be expressed by

$$P_c = \left(\frac{3}{2\pi}\right)^{3/2} \frac{\upsilon_s}{\langle r^2\rangle^{3/2}}$$

and P_2, the probability of intermolecular condensation leading to a dimer, by

$$P_2 = N\frac{\upsilon_s}{V} = \frac{N_A C}{M}\upsilon_s$$

with C the concentration of polymer (g/mL), M the molar mass, $\langle r^2\rangle$ the mean square end-to-end distance, υ_s the volume in which the reaction between A and B takes place, N the number of macromolecules, N_A Avogadro's number, and V the volume of solution. The ratio between cyclic and polycondensates is thus given by

$$\frac{P_c}{P_2} = \left(\frac{3}{2\pi\langle r^2\rangle}\right)^{3/2} \frac{1}{N_A[C^*]}$$

where [C*], the concentration of active ends, is equal to C/M.

For polystyrene we may consider,[1] in a θ solvent; $\langle r^2\rangle = 4.74 \times 10^{-17}$ M and, in a good solvent, $\langle r^2\rangle = 1.14 \times 10^{-17}$ M.[1,14]

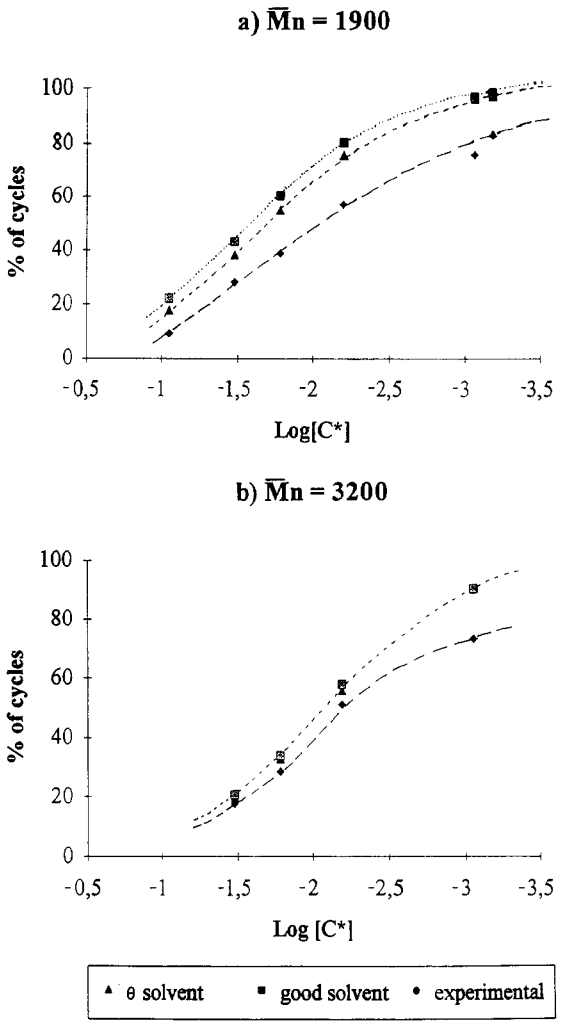


Figure 7. Theoretical and experimental variations of the percent of cyclized polystyrene with respect to log [C*]: (a) $\bar{M}_n$ = 1900; (b) M_n = 3200.

The theoretical percentages of cyclics expressed by 100-$[P_c/(P_c + P_2)]$ are plotted versus the concentration of polystyrene chains in Figure 7a,b for polystyrene precursors of $\bar{M}_n$ = 1900 and 3200, respectively. As may be seen, in the molecular weight range examined, there is no strong predicted effect of the nature of the solvent on the theoretical cyclization yields.

Cyclization experiments were performed at various α,ω-heterodifunctional polystyrene concentrations, ranging from 10^{-2} to 10^{-4} M. The resulting polymer mixtures were analyzed by GPC as indicated before. A series of GPC traces are presented in Figure 8. A shift of the GPC trace of the linear precursor toward a higher elution volume, corresponding to the formation of cyclic polystyrenes, as well as the formation of polycondensates, in increasing proportion with the higher active center concentration, is observed. The percentages of cyclics and polycondensates formed for two polystyrene precursors of different $\bar{M}_n$ are given in Table 4. As predicted by the theory, for the same precursor concentration, the percentage of cycles decreases with increasing precursor chain length. For the higher [C*] values, $\langle G_{exp}\rangle$ is very high. This may be explained by a shift of the peak corresponding to cyclics due to the high percentage of polycondensates formed in these conditions.

The evolution with dilution of the percentage of cyclics, determined from experiment and predicted by the theory, may be compared in Figure 7a,b. A relatively good agreement is observed between the two curves. One can

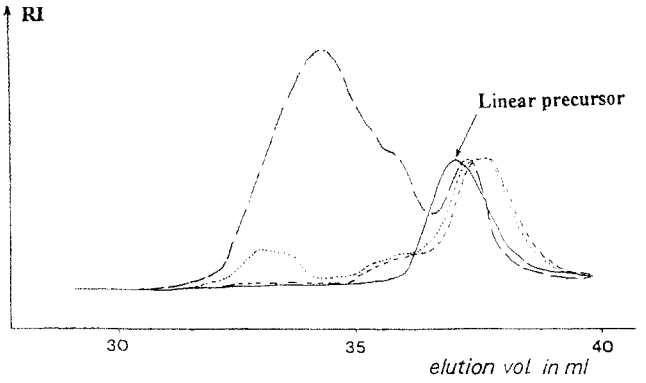


Figure 8. GPC curves of different α,ω-polystyrene mixtures recovered after treatment of the linear polymer precursor with $SnCl_4$/toluene: (—) PS precursor ($\bar{M}_n$ = 1900). Polymer concentration: (- - -) [C*] = 8.8×10^{-4} M; (· · ·) [C*] = 6.3×10^{-3} M; (– – –) [C*] = 8.8×10^{-2} M.

Table 4. Influence of the Concentration of Active Ends ([C*]) on the Percentage of Cycles Formed

		theoretical % of cycles[a]			
$\bar{M}_n$ of precursor	[C*] 10^{-3} M	θ solvent	good solvent	% of cycles[b]	$\langle G_{exp} \rangle$[c]
1900	88	18	22	9.5	0.95
	32.9	38	43	28	
	16.4	55	60	39	
	6.27	76	80	57	0.88
	0.88	96	96.5	76	0.83
	0.66	97	97.5	83	0.82
3200	32.9	19.7	21	18	0.92
	16.4	33	34	28.5	0.85
	6.27	56	58	51	0.84
	0.88	90	90	73	0.82

[a] Calculated from Jacobson–Stockmayer. [b] Calculated from the GPC peak areas ratio, cyclics/crude product. [c] Ratio of the apparent molecular weights derived from GPC signals attributed to cyclics and linear precursors.

notice, however, that the percentage of cycles formed is slightly lower than predicted, in particular in highly diluted conditions. One possible reason could be the contribution of side reactions, such as the de-activation of one end of the precursor, which would then allow it only to dimerize. This might also come from the quite low molecular weight samples used in the cyclization study, whereas the Jacobson–Stockmayer[13] theory applies mainly for high molecular weight polymers.

Further works are in progress to extend this cyclization technique to the preparation of polystyrenes of higher molecular weight as well as to the synthesis of macrocyclic polymers and copolymers of various structures.

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(14) It is worthy to note that the Jacobson–Stockmayer theory applies mainly to high molecular weight polymers. Therefore, cyclization yields calculated in the case of low molecular weight samples should be considered only as a rough estimate, however, useful for comparison with experimental data.