α-Acetal-ω-bis(hydroxymethyl) Heterodifunctional Polystyrene: Synthesis, Characterization, and Investigation of Intramolecular End-to-End Ring Closure

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ABSTRACT: A route to macrocyclic polystyrene of controlled dimensions based on a new ring closure process has been investigated. It involved the direct coupling of an α-acetal,ω-bis(hydroxymethyl) heterodifunctional linear polystyrene precursor previously prepared by living anionic polymerization. Cyclization was achieved under high dilution, by intramolecular condensation of the polymer ends in the presence of a mild acid as catalyst. Macrocyclic polystyrenes were prepared directly in high yield (>90%) without any necessary fractionation step. The synthesis and structural characterization of both the linear α,ω-heterodifunctional precursors and the corresponding cyclized polystyrenes, as well as a preliminary investigation of their stability and specific thermal properties, are reported.

Introduction

The synthesis of cyclic polymers with well-controlled molar masses and narrow molar mass distributions and the study of their physical properties has attracted considerable interest in recent years.[1,2] Although new strategies have been proposed recently, anionic polymerization has been the most generally used end-to-end polymer cyclization method.[1−8] In the anionic process, the strategy is to form living difunctional polymer precursors with two carbanionic ends and to couple them intramolecularly under high dilution with a stoichiometric quantity of a difunctional electrophile. Recent advances in analytical techniques[8,9] have demonstrated that side reactions occur, with the final cyclized product containing uncyclized precursor and linear polycondensates fractions.

We and others recently developed a different approach that involves the direct intramolecular end-to-end coupling of a heterodifunctional linear polymer precursor with two complementary reactive end groups.[10−17] In this case, the reaction is unimolecular and does not need a coupling agent. The ring closure may involve coupling reactions based either on deactivation of cationic-like propagating species or on more conventional organic addition or substitution reactions.

The present study investigates the synthesis of cyclic polystyrene chains by intramolecular formation of an acetal linkage, starting with an appropriate heterodifunctional linear precursor. The strategy used, the synthesis, and characteristics of the linear and cyclic polystyrene chains are presented.

Experimental Section

Materials. Benzene (99.5%, J. T. Baker, The Netherlands) was purified by distillation from calcium hydride and stored in glass vessels over polystyryllithium seeds. Styrene (99%, Sigma-Aldrich France) was purified by distillation from calcium hydride at reduced pressure and stored until use in glass flasks fitted with PTFE stopcocks over dibutylmagnesium (3 vol % relative to monomer of a 1 M cyclohexane solution). 1,1,1-Tris(hydroxymethyl)propane (99%, Sigma-Aldrich France) was used as received. Chloropropionaldehyde diethyl acetal (99%, Sigma-Aldrich France) was dried over calcium hydride and distilled under vacuum just before use.

Synthesis. Isopropylidene-2,2-bis(hydroxymethyl)-1-(1-chloroethoxyethoxy)butane (2). It was prepared in two steps from 1,1,1-tris(hydroxymethyl)propane.

(a) Synthesis of Isopropylidene-1,1-bis(hydroxymethyl)-1-hydroxymethylpropane. 1,1,1-Tris(hydroxymethyl)propane (10.0 g 75 mmol) was dissolved in acetone (100 mL) acidified by 4 to 5 drops of an aqueous solution of HC1 (12 N) and stirred for several hours at room temperature. After addition of sodium carbonate (10 g), the solution was filtered and acetone was distilled off, yielding isopropylidene-1,1-dihydroxymethyl-1-hydroxymethyl propane. The latter was dried under vacuum and stored over molecular sieves. Yield: 9.5 g. ^{1}H NMR: aluminate (δ = 0.8 (t, CH_3), 1.2−1.4 (q, CH_2 and d, CH_3), 2.3 (s, OH), 3.5−3.8 (m, CH_2O).

(b) Isopropylidene-2,2-bis(hydroxymethyl)-1-(1-chloroethoxyethoxy)butane (2) was prepared according to ref 18. Isopropylidene-1,1-bis(hydroxymethyl)-1-(hydroxymethyl)-propane (7 g, 40 mmol) and tetrabutylammonium hydrogen sulfate (13 g, 40 mmol) were dissolved in bis(chloroethyl)ether (100 mL). The mixture was poured into a 50% aqueous sodium hydroxide solution (100 mL) and vigorously stirred for 24 h at room temperature. After addition of dichloromethane (100 mL) and water (100 mL), the organic phase was washed with water, dried with magnesium sulfate, filtered, and concentrated under vacuum. The product **(2)** was finally recovered and purified twice by distillation under vacuum in the presence of CaH_2. Yield: 6 g. ^{1}H NMR: δ = 0.8 (t, CH_3), 1.2−1.4 (q, CH_2 and d, CH_3), 3.5−3.8 (14H m,CH_2O and CH_2Cl).

Polymerizations. Polymerizations were performed under vacuum in glass flasks equipped with PTFE stopcocks. Fresh 3-lithiopropionaldehyde diethylacetal prepared as previously described[11,12] was used to initiate styrene polymerization in benzene to yield living α-diethyl acetal polystyryllithium **(1)**. Heterodifunctional polystyrene **(3)** was obtained by deactivation of living polystyrene **(1)** with **(2)**. In a typical example the living α-acetal polystyrene **(1)** ($\bar{M}_n$ = 1750 g/mol, 5 g) in benzene (100 mL) was deactivated by adding neat isopropylidene-2,2-bis(hydroxymethyl)-1-(1-chloroethoxyethoxy)butane **(2)** in excess (1.6 g, 5.7 mmol) with respect to living chains. Immediate transformation of polystyrene ends was shown by the rapid change of the medium to colorless. The resulting polymer was recovered by partial solvent evaporation followed by precipitation of the concentrated polymer solution into methanol. After redissolution in dichloromethane (100 mL), the organic layer containing the polymer was washed

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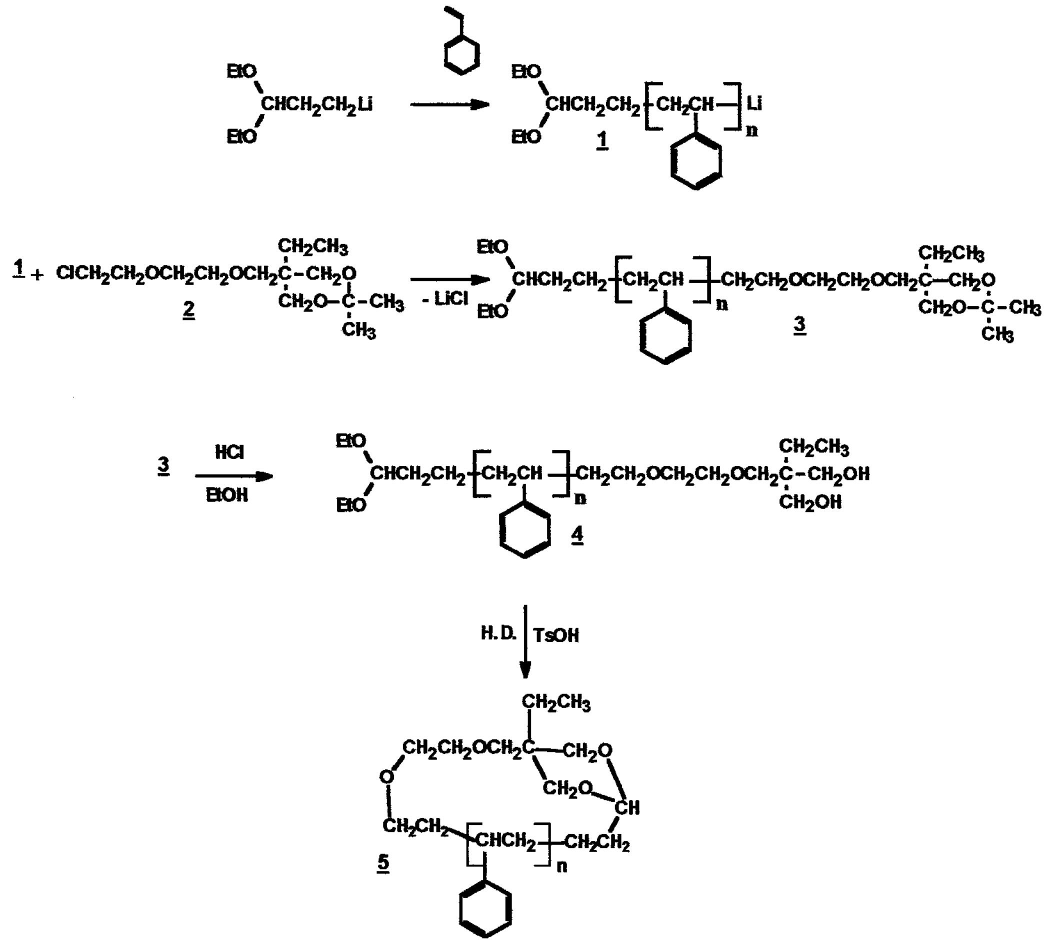
Scheme 1



with water, concentrated, precipitated into methanol and dried under vacuum to give **(3)** as a white powder (Yield: 4.5 g, 90%. $\bar{M}_n = 1820$ g/mol; $\bar{M}_w/\bar{M}_n = 1.08$).

Preparation of Heterodifunctional Polystyrene (4). Polystyrene **(3)** (5 g, 27 mmol) was dissolved in dichloromethane (200 mL) and ethanol (50 mL) containing 4 to 5 drops of aqueous HCl (12 N). The mixture was stirred vigorously at room temperature for 5 h. The organic phase was then washed with 5% sodium hydroxide (300 mL) and water (500 mL) and finally dried over $MgSO_4$. After solvent evaporation polymer **(4)** was recovered by precipitation into methanol. (Yield: 4.5 g, 90%. $\bar{M}_n = 1800$ g/mol. $\bar{M}_w/\bar{M}_n = 1.08$.)

Cyclization. The heterodifunctional polystyrene **4** (2 g, 1 mmol) was dissolved in CH_2Cl_2 (100 mL), and the solution was placed in a dropping funnel. The polymer solution was then added dropwise (over 5−6 h) to a large volume of CH_2Cl_2 (600 mL) containing *p*-toluenesulfonic acid (TSOH) (200 mg, 1 mmol) and allowed to stand for 30 min at room temperature. Then 3% aqueous sodium hydroxide (300 mL) was added under vigorous stirring to neutralize the mixture. The organic solution was washed with water (500 mL) and the cyclized polymer **(5)** was recovered as a white powder after solvent evaporation and precipitation into cold methanol. (Yield: 1.8 g, 90%. $\bar{M}_{n(app)} = 1420$ g/mol; $\bar{M}_w/\bar{M}_n = 1.10$).

Ring-Opening Experiments. Acetal-linked cyclic polystyrene ($\bar{M}_{n(app)} = 3250$ g/mol, $\bar{M}_w/\bar{M}_n = 1.15$, 1 g, 0.3 mmol) was dissolved in a methylene dichloride/propylene glycol (100 mL) mixture (90/10 v/v). Then 0.5 mL of HCl 12 N was added, and the solution was vigorously stirred for 72 h at 20 °C. The reaction mixture was then neutralized by sodium carbonate and washed with water, and the polymer was recovered by precipitation into methanol. ($\bar{M}_n = 3250$ g/mol; $\bar{M}_w/\bar{M}_n = 1.20$.)

Characterization. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker AC 200FT apparatus. SEC analysis was performed at 20 °C in THF (0.7 mL/min), on a Varian apparatus equipped with refractive index/UV dual detection and fitted with four TSK columns (250, 1500, 10^4, 10^5 Å). Polystyrene molar masses were determined by using linear polystyrene as calibration standards. A trace of hydroquinone 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 from the second heating cycle (10 °C/min). MALDI−TOF spectra were recorded on a micromass TOFSTEC apparatus (Manchester, U.K.). The instrument is equipped with a pulsed N2 laser (337 nm, 4 ns pulse width) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron mode and with an accelerating voltage of 20 kV.

Polymer samples were dissolved in THF at 10 mg/mL. The dithranol matrix solution was prepared by dissolving 10 mg of sample in 1 mL of THF and the solution of cationization agent by dissolving NaI in MeOH. The solutions were combined in a 10:1:1 volume ratio of matrix to polymer to cationization agent. Here, 1−2 μL of the obtained solution was deposited onto the sample target and air-dried. The presence of Li^+ cation in some polymer samples can be attributed to residual LiCl formed during living PSLi deactivation.

Results and Discussion

Cyclic polystyrenes **(5)** were prepared in an overall cyclization yield higher than 90% from the linear α-diethyl acetal-ω-bis(hydroxymethyl) heterofunctional polystyrene precursors **(4)** by the three-step procedure described in Scheme 1. Linear precursors were synthesized first by living anionic polymerization of styrene using 3-lithiopropionaldehyde diethyl acetal as an initiator,[11,12] and isopropylidene-2,2-bis(hydroxymethyl)-1-(2-chloroethoxyethoxy)butane **(2)** as a functional chain

Table 1. Characteristics of Linear Heterodifunctional α-Diethylacetal-ω-bis(hydroxymethyl) Heterodifunctional Polystyrenes and of the Corresponding Polystyrene Macrocycles Obtained by Intramolecular End-to-End Acetal Ring Closure

DP_n	chain arch.	$M_{n(th)}$ $\times 10^{-3}$ [a] (g/mol)	M_{peak} $\times 10^{-3}$ [b] (g/mol)	$M_{n(exp)}$ $\times 10^{-3}$ [c] (g/mol)	$\bar{M}_w/\bar{M}_n$	$\langle G_{exp}\rangle$ [d]	T_g (°C)
13	lin	1.94	2.0	1.7	1.08		15
	cycl.		1.5	1.4	1.10	0.75	76
33	lin	4.02	5.0	3.9	1.15		49
	cycl.		3.9	3.2	1.15	0.78	96
62	lin	6.40	7.5	6.9	1.03		89
	cycl.		6.0	5.4	1.06	0.80	101
106	lin	1.20	12.0	11.5	1.03		97
	cycl.		9.5	9.6	1.03	0.79	102
306	lin	2.64	32.0	31.2	1.02		104
	cycl.		25.8	26.6	1.08	0.81	105

[a] Determined from the initial molar ratio [styrene]/[3-lithiopropionaldehyde diethylacetal]. [b] Apparent peak molar mass determined by SEC using linear polystyrene standards. [c] Determined by SEC on the basis of linear polystyrene standards. [d] Ratio of the apparent peak molar masses (M_{peak}) derived from SEC traces of cyclics polystyrene and their linear precursors.

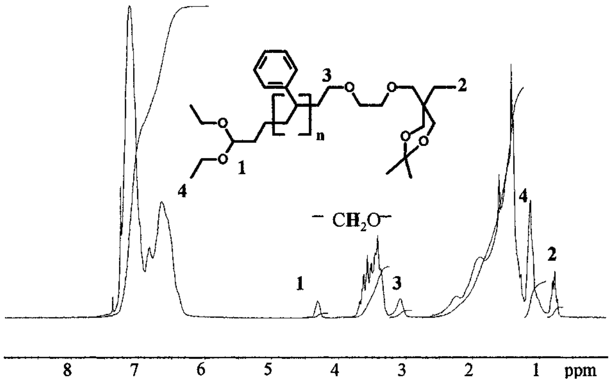


Figure 1. 200 MHz Proton NMR spectrum ($CDCl_3$) of a linear heterodifunctional α-diethylacetal-ω-isopropylidene-2,2-bis(hydroxymethyl)polystyrene ($\bar{M}_n$ = 1750).

terminating agent. The dimensional characteristics of the various α,ω-heterodifunctional linear polystyrenes are summarized in Table 1. The experimental and theoretical polystyrenes $\bar{M}_n$, calculated on the basis of complete initiation of styrene polymerization by the lithio acetal derivative agree well, and molar mass distributions (MWD ≤ 1.15) are narrow. A proton NMR spectrum and the peak assignments of an α,ω-heterodifunctional polystyrene of low molar mass ($\bar{M}_n$ = 1750) are shown in Figure 1. The relative number of α-diethylacetal and ω-propylenediol end groups per polystyrene chain was determined from the relative area of the acetal resonance (1) (δ = 4.3 ppm) and the methyl (2) (δ = 0.8 ppm) or methylene resonances (3) (δ = 3.1 ppm). For samples with $\bar{M}_n$ < 10 000, the ratio between the diethylacetal head and isopropylidene-2,2-bis(hydroxymethyl) end groups was very close to 1, which indicates that the formation of the targeted heterodifunctional polystyrene chains was quantitative. For polystyrene with $\bar{M}_n$ of 30 000, the end functionality could not be estimated directly by NMR. In this case, the SEC trace shows a small portion of a high molar mass fraction, which may be attributed to a side coupling reaction (peak II, Figure 3).

The cyclic ω-isopropylidene-2,2-bis(hydroxymethyl) acetal function was selectively hydrolyzed under mild acidic conditions in a dichloromethane–ethanol mixture in the presence of a small amount of aqueous HCl. The large excess of ethanol stabilizes the linear α-diethylacetal group and avoids its transformation into a reactive aldehyde function during the cleavage of the terminal cyclic acetal, thus yielding selectively α-diethylacetal-ω-bis(hydroxymethyl)polystyrene. The quantitative ω-chain end derivatization was confirmed by thin-layer chromatography. Using THF/heptane (40/60%, v/v) as the eluent, the ω-dihydroxyfunctionalized polystyrene **(4)**, with its two primary hydroxy groups, migrates much slowly than its non-ω-difunctional precursor.

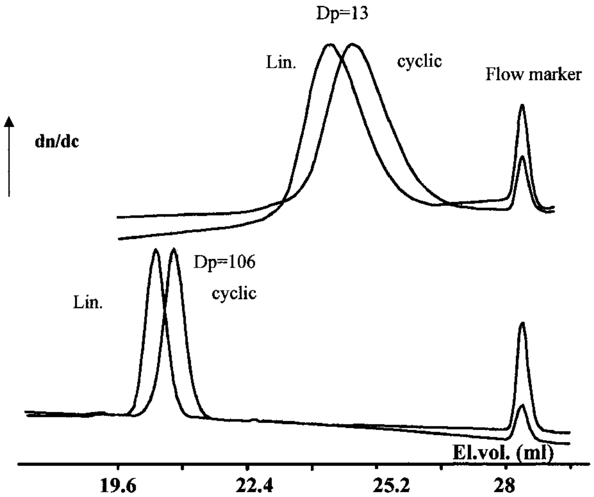


Figure 2. SEC curves of linear heterodifunctional α-diethylacetal-ω-isopropylidene-2,2-bis(hydroxymethyl)polystyrene ($\bar{M}_n$ = 1750 and 11 500) and their corresponding crude cyclized products.

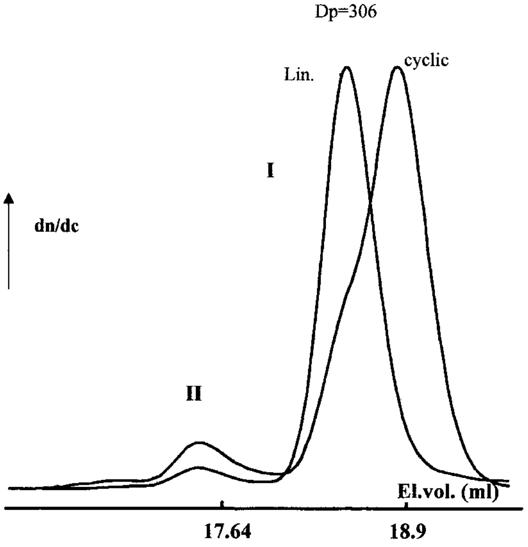


Figure 3. SEC curves of linear heterodifunctional α-diethylacetal,ω-isopropylidene-2,2-bis(hydroxymethyl)polystyrene ($\bar{M}_n$ = 31 200) and the corresponding crude cyclized product.

This polystyrene is cyclized by directly coupling the two complementary α-and ω-functional chain ends in acidic media. This strategy is similar to the one described previously for the cyclization of α-diethylacetal-ω-styrenyl heterodifunctional polystyrene and poly(chloroethyl vinyl ether) chains,[10–16] except that the present end-coupling reaction forms a cyclic acetal linking unit. This acetalation takes place quantitatively under very mild conditions. Its driving force is formation of a six-membered acetal ring, which forms more easily and is more stable than linear acetals (Scheme 1).

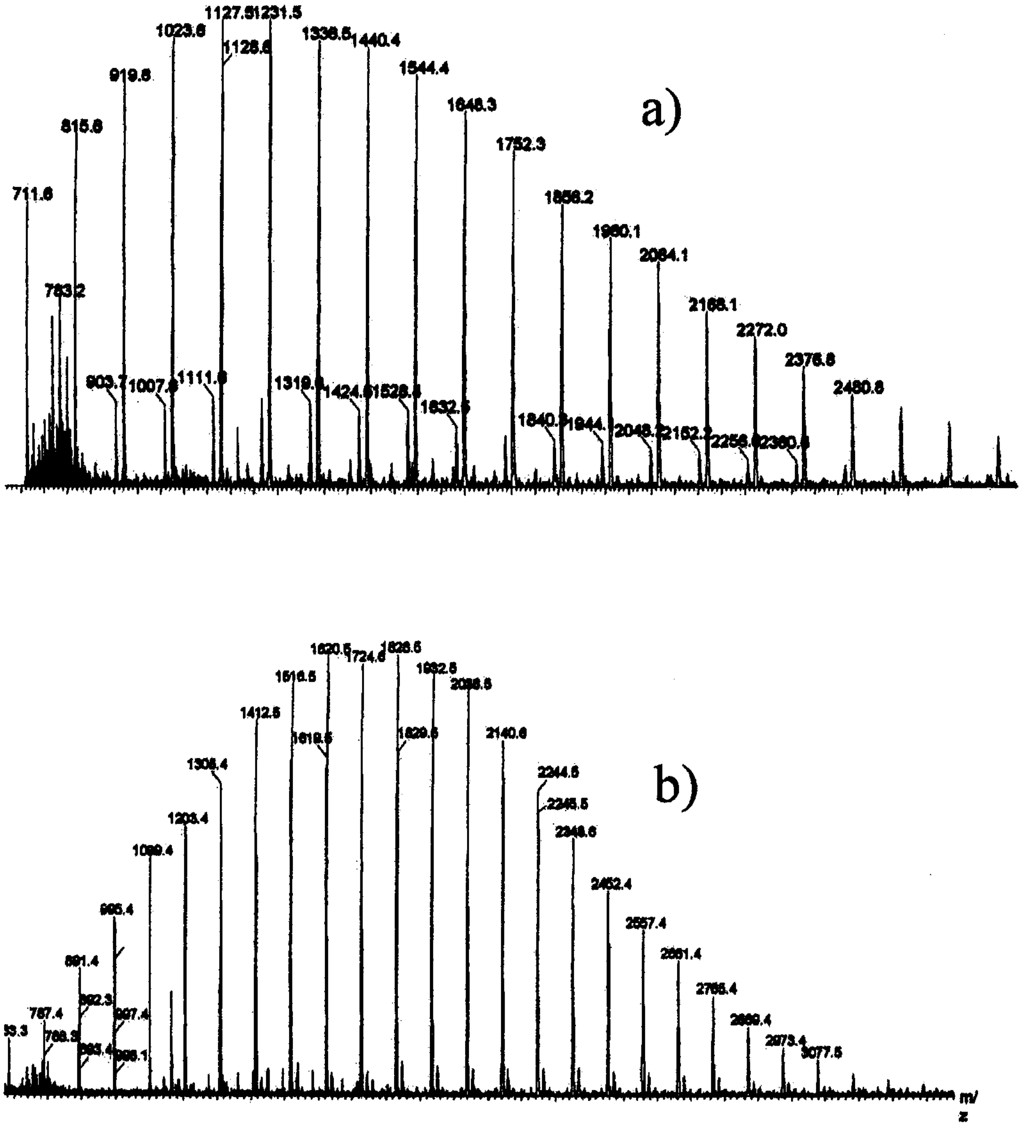


Figure 4. MALDI−TOF spectra of linear heterodifunctional α-diethylacetal,ω-isopropylidene-2,2-bis(hydroxymethyl)polystyrene (M_L + Na, $\bar{M}_{n(SEC)} = 1750$) (a) and the corresponding crude cyclized product (M_c + Na) (b). The small peaks in part a correspond to the M_L + Li series.

Intramolecular cyclization of **4** was performed under high dilution, by slowly adding a solution of the linear polystyrene precursor into a large volume of dichloromethane containing *p*-toluenesulfonic acid (TsOH) as catalyst (final concentration in polystyrene chains in the solution = (3−4) × 10^{-4} mol/L). The crude SEC traces of two cyclized polystyrene samples **(5)** ($\overline{DP}_n = 13$) and ($\overline{DP}_n = 106$) are presented in Figure 2, together with those of the corresponding linear precursors **(3)**. As expected, the cyclized polymers elute at higher volume than the linear precursors. The ratio between the two SEC signals Mp_c/Mp_l, $\langle G \rangle = 0.77-0.80$ (see Table 1), agree well with $\langle G_{exp} \rangle$ already reported for macrocyclic polystyrenes.[2,11,13,21] The slightly higher value observed for the polystyrene with $\bar{M}_n = 31\,200$ g/mol ($\langle G_{exp} \rangle = 0.8$) (Figure 3), can be attributed to the presence of uncyclized linear precursor (10−20%) which is detected by a slight shoulder at lower elution volume on the main polymer SEC signal. Linear PS may be unreacted because end functionalization of the precursor was incomplete, probably due to traces of impurities in the experimental polymerization conditions used. However, samples with lower $\bar{M}_n$ had no detectable linear polystyrene contaminant in their SEC traces ($\langle G_{exp} \rangle = 0.77-0.79$), indicating high cyclization yields.

The structure of the linear and cyclized polystyrene was further characterized using MALDI−TOF.[19] According to the targeted structures, the linear α,ω-polystyrene precursor should exhibit calculated mass numbers respectively of $M_L + Na^+$(or Li^+) = (376 + 104*n*) + 23(or +16) and the corresponding cyclic $M_C + Na^+$(or Li^+) = (244 + 104*n*) + 23 (or +16). The difference arises from the end-linking unit. The experimental mass numbers are in excellent agreement with the calculated values for both the linear and cyclic polymers. MALDI−TOF spectra of a linear α,ω-heterodifunctional polystyrene precursor ($\bar{M}_n = 1750$ g/mol) and the corresponding acetal-linked macrocyclic polystyrene are presented in Figure 4. The spectra show two peak series (Na^+ and Li^+) for the linear and one peak series for the cyclic polystyrenes (Na^+), in agreement with a clean and complete end chain functionalization of the linear and

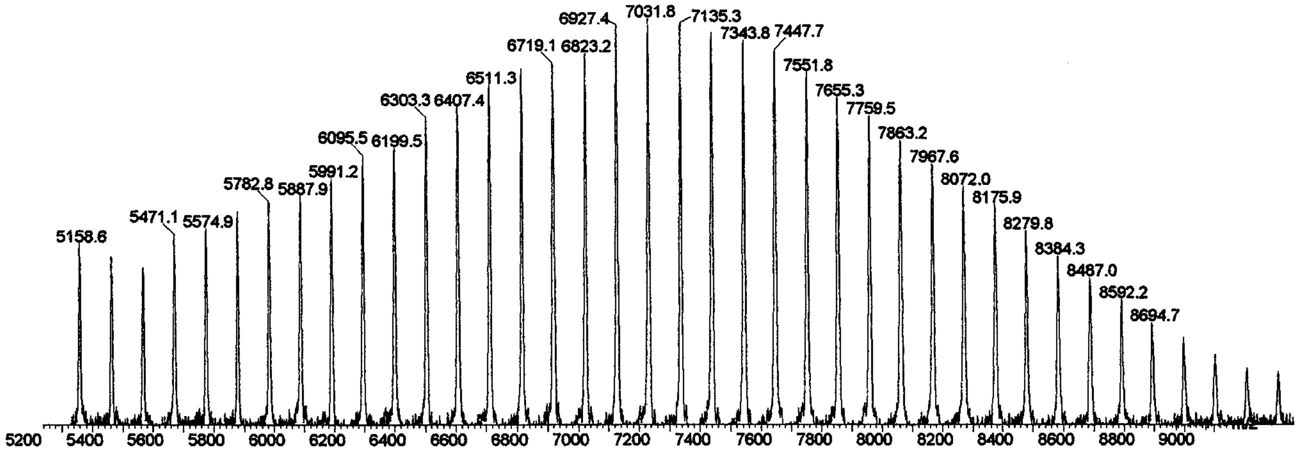


Figure 5. MALDI−TOF spectrum of cyclic acetal-linked polystyrene (M_L + Na, $\bar{M}_{n(SEC)} = 6900$).

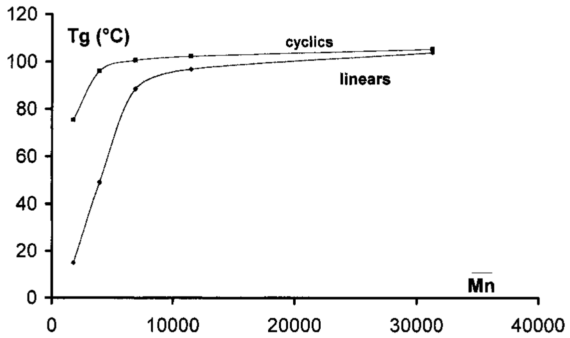
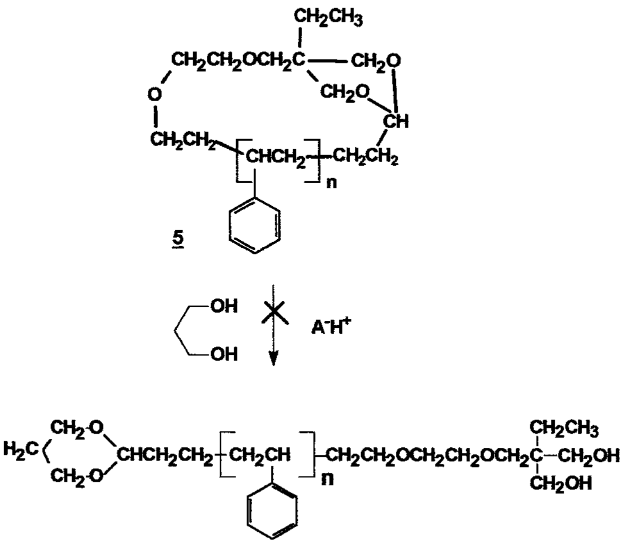


Figure 6. Glass transition temperatures of linear α-diethylacetal,ω-isopropylidene-2,2-bis(hydroxymethyl)polystyrenes and of the corresponding acetal-linked cyclics of increasing molar masses.

Scheme 2



a quantitative ring closure process. This is also true for the polystyrene sample with $\bar{M}_n = 6900$ g/mol (Figure 5).

The glass transition temperatures of the heterodifunctional linear polystyrenes and the acetal-linked cyclics of different molar masses are summarized in Table 1. The variations of T_g with increasing polystyrene molar mass are plotted in Figure 6. The loss in chain mobility by cyclization results in higher T_g's for cyclics. However, for very low molar mass oligomers, T_g decreases for both linears and cyclics with decreasing polymer molar mass. This agrees with our previous findings,[2,12] as well as the more recent literature data.[6,20,21] Note also the T_g's for the linear low molar mass PS samples are much lower than reported in previous study whereas very similar values are found for the cyclics.[12] This may be attributed to the presence of the soft oligoether segment at the chain termini.

Since the acetal linkage may in principle ring-open under acidic conditions and re-form linear chains (Scheme 2), we investigated the reversibility of the cyclization process. Solutions of the acetal-linked cyclic polystyrene in methylene chloride and ethanol or propylene glycol mixtures were acidified and allowed to react at 20 °C for 24 h. We did not observe any changes in the SEC traces after treatment with various acids such as TsOH, Amberlyst A15 (strong acid resin), or HCl. SEC and MALDI−TOF analyses of the recovered polystyrenes were consistent with the cyclic structure, which demonstrates that the cyclic acetal link is stable.

Further use of this nearly quantitative cyclization procedure for the preparation of partially deuterated cyclic polystyrene-H-*b*-polystyrene-D and polystyrene-D-*b*-polyisoprene copolymers is in progress.

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