Controlled Synthesis of Bicyclic "Eight-Shaped" Poly(chloroethyl vinyl ether)s

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ABSTRACT: The synthesis of bicyclic eight-shaped poly(chloroethyl vinyl ether)s of controlled molar masses and narrow polydispersities has been achieved in very good yield. The strategy used is derived from the one reported for the synthesis of monomacrocyclic poly(vinyl ether)s and polystyrene. The procedure consists in the preparation of a linear tetrafunctional precursor bearing two series of antagonist functions, namely, α,α'-distyrenyl-ω,ω'-diacetal-poly(CEVE). The synthesis and the characterization of this polymer by controlled living cationic polymerization of chloroethyl vinyl ether are first described. In a second step, performed in highly diluted conditions, the acetal ends of the precursor are selectively activated by an electrophilic catalyst in order to form carbocationic-like termini which rapidly add on the styrenyl function of the chain. The presence of two functions of each type on a poly(CEVE) chain allows the formation of two rings per chain. The structural investigation of the cyclized polymer by SEC and NMR supports that bicyclic eight-shaped poly(CEVE) can be prepared cleanly and almost quantitatively by this cyclization procedure based on unimolecular end-to-end coupling reactions.

Introduction

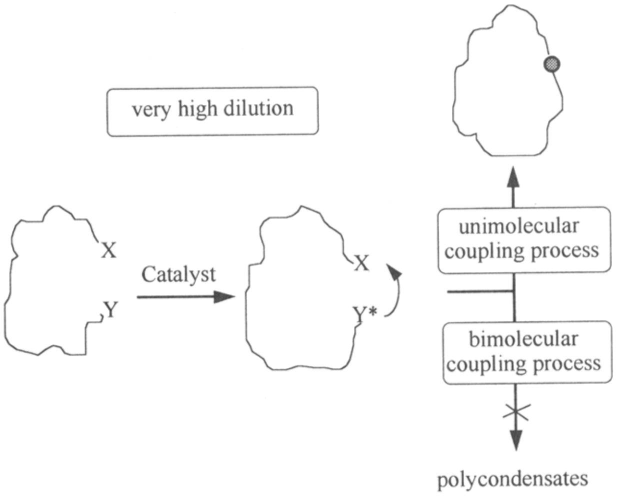
The synthesis and the study of polymers with a macrocyclic chain architecture are a very active research domain in polymer science.[1−29] Indeed, from both theoretical considerations and available experimental data, it may be expected that end-to-end cyclization of a polymer chain will noticeably modify its intrinsic solution and bulk properties. In the case of more complex multicyclic structures,[30] it has already been shown that new and very specific properties such as the complexation and the transport of organic molecules[31] can also be reached by such type of constrained ring-type architecture.

If we do not consider macrocycles of broad size distribution obtained from polymer systems in which an equilibrium exists between linear chains and cyclics,[8,13,21] only a very limited number of macrocyclic polymers with controlled ring dimensions and narrow polydispersity have been synthesized so far, despite the continuous efforts made over the past decade to optimize and extend the routes toward this category of macromolecules.

Until recently, ring-shaped polymers were almost exclusively prepared by the end-to-end coupling of linear living polymers by dielectrophilic molecules in highly diluted solutions.[1−7,9−12,14−20,22−24,29]

A quite different approach to chain cyclization, based on an unimolecular end-to-end coupling process, has been proposed recently.[25−28] It involves first the formation of an α,ω-heterofunctional polymer precursor by living-type polymerizations. The precursor is then cyclized under high dilution after selective activation of one of its end functions, to allow its addition onto the other polymer chain end. The ring-closure strategy is shown in Scheme 1. First applied in the case of linear precursors obtained by living cationic polymerization, i.e., poly(vinyl ether)s,[25,26] this technique was then extended to living anionic polymerization systems.[27,28] The improvement of the cyclization procedure and the optimization of the reaction conditions allow the preparation of cyclic polystyrenes with yields almost quantitative and higher than 90%.[28] The use of tedious fractionation techniques generally required with other cyclization routes to get pure cyclics is not necessary with this procedure.

Scheme 1. Formation of Macrocyclic Polymers by Direct End-to-End Ring Closure



The high selectivity in the ring formation encouraged us to further investigate the synthesis of more complex macrocyclic structures. Among these the preparation of macrotricyclic poly(chloroethyl vinyl ether)s has already been described.[30] It was observed that these cage-like macromolecules exhibit very interesting complexation properties toward organic salts and large molecules such as dyes and porphyrins,[31] whereas the corresponding star, monocyclic, and linear poly(chloroethyl vinyl ether) architectures do not. However, the procedure used for the synthesis of tricyclic polymers is quite difficult and, moreover, the reproducibility of the experiments remains fairly low. To optimize the synthetic routes leading to polymers with a plurimacrocyclic chain architecture as well as to identify the structural parameters which contribute to the complexation ability of the pluricyclic poly(chloroethyl vinyl ether)s, the synthesis of bicyclic poly(chloroethyl vinyl

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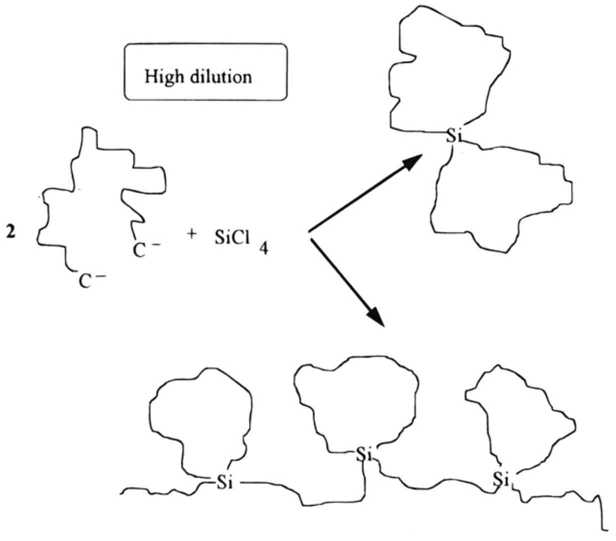
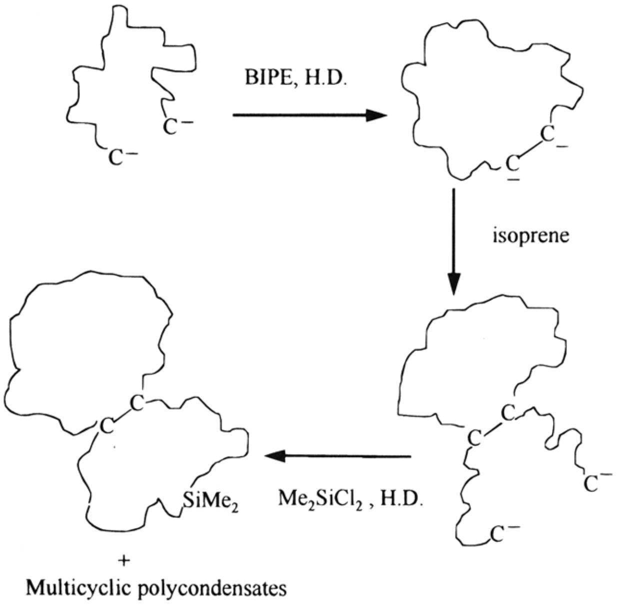
Scheme 2. Synthesis of Bicyclic Polystyrene[18] and Polyisoprene,[20] with Accompanying Polycondensates, Obtained by Bimolecular Coupling with $SiCl_4$



Scheme 3. Synthesis of Bicyclic Polyisoprene by Successive Bimolecular Coupling of Living Difunctional Chains[29]



BIPE : bis(isoprenyl-4-phenyl)ethane

ether)s with an eight-shaped chain topology has been investigated.

Several studies concerning the synthesis of eight-shaped macromolecules have already been reported.[18,20,29]

The first route involves the coupling of two bifunctional polymer chains (polystyrene,[18] polyisoprene[20]) onto—and per—$SiCl_4$ molecule (Scheme 2). With polystyrene, a multimodal molar mass distribution was obtained, with a major high molecular weight fraction composed of polycondensates, likely containing polycyclic structures. The lower molecular weight fraction, present in small proportion, was attributed to bicyclic polystyrene. In the case of polyisoprene dicyclization,[20] higher yields, around 60%, could be reached, in agreement with a better control of the ring-closure process.

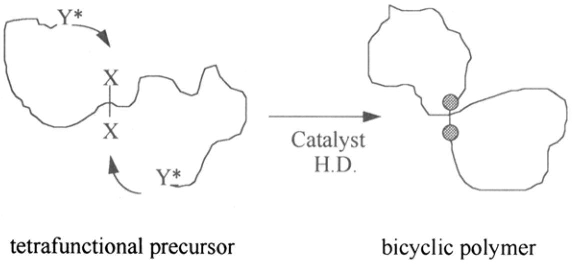
A different approach also based on a bimolecular end-to-end chain coupling has been reported recently.[29] The strategy is described in Scheme 3. The α,ω-poly(diisoprenyllithium) precursors are first (mono)cyclized in the presence of a stoichiometric amount of 1,2-bis(4′-isopropenylphenyl)ethane (BIPE); the so-formed monomacrocyclic bis(α-methylstyryl)lithium) salt is then used as a bifunctional initiator for a new isoprene polymerization. Finally, the monocyclic polyisoprene with two end-functional arms is cyclized a second time by adding $(CH_3)_2SiCl_2$. Yields in the desired bicyclic polymer are in the range 60−70%, yet a noticeable fraction of polycondensation products is still present. Further characterization of the chemical and physical properties of these original bicyclic macromolecules has not yet been reported.

A different method for the synthesis of polymers with a bicyclic chain architecture has been investigated. The strategy, the cyclization yields, and the first structural characterization of bicyclic poly(chloroethyl vinyl ether)s are reported in this paper.

Results and Discussion

The strategy developed for the preparation of eight-shaped bicyclic poly(chloroethyl vinyl ether)s is derived from the one previously used for monocyclic polymers.[25−28] As shown in Scheme 4, it involves first the controlled synthesis of a linear tetrafunctional polymer precursor of precise dimensions bearing two types of complementary functionality. In a separated stage, performed under extreme dilution, one type of function is then selectively activated to allow its reaction with the complementary functional group of the same chain, thus leading to ring formation. As before, for the synthesis of monocyclic polystyrene and poly(chloroethyl vinyl ether)s, the activated functions are acetal end groups, whereas the complementary ones are styrenyl groups.

Scheme 4. Strategy for the Synthesis of Bicyclic Polymers by Unimolecular Ring Closure

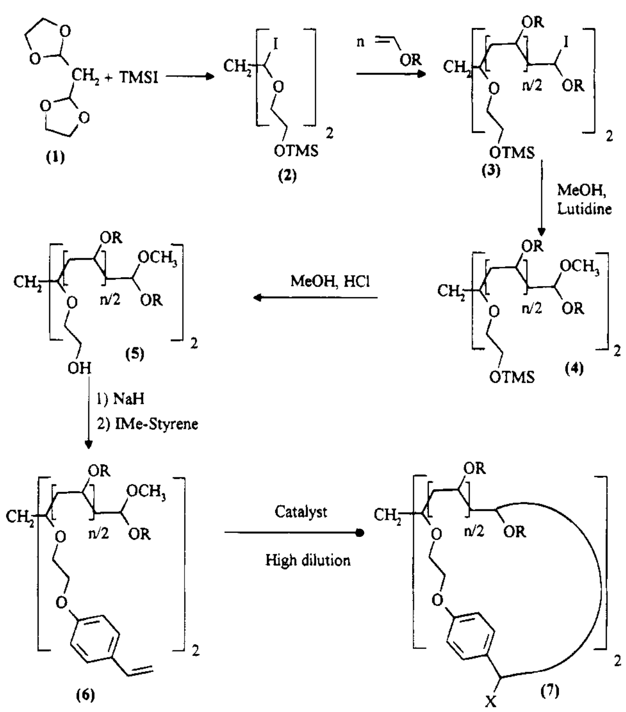


The synthesis and structural characterization of the corresponding tetrafunctional polymer precursor are first examined. The cyclization procedure as well as some characteristics and properties of the bicyclized poly(CEVE) chains will then be reported.

I. Synthesis of the Tetrafunctional Linear Chain Precursors. Since the precise control of the initiation, propagation, and termination steps of the polymerization is essential, the preparation of linear α,α′-distyrenyl-ω,ω′-diacetal-poly(CEVE)s was achieved by controlled "living" cationic polymerization of CEVE. The reaction pathway used to accede to the desired polymer structure is described in Scheme 5. It involves successively the following:

(a) Functional Initiation. It has been shown recently[32,33] that the reaction of cyclic acetals with trimethylsilyl iodide (TMSI) leads selectively to α-iodo ether derivatives bearing a hydroxy-protected function. This method allows the introduction of an OH group at the head of a poly(vinyl ether) chain which is grown from this adduct.

Scheme 5. Strategy Used for the Synthesis of Bicyclic Poly(CEVE)



Since in the strategy adopted for the synthesis of bicyclic polymer two hydroxy head groups as well as two terminal chain ends, corresponding to a bifunctional chain growth, were required to give the desired linear precursor structure (**6**), 1,1′-methylenebis(dioxolane) (**1**) was used as a chain starter. Its reaction with TMSI gives the diiodo ether derivative (**2**) from which the CEVE polymerization is initiated. The proton NMR spectrum of the diiodo adduct (**2**) as well as the corresponding peak assignments are presented in Figure 1.

(b) Propagation. To ensure a living-type CEVE polymerization apt to lead to end-functional poly(CEVE) (**3**), the polymerization was performed at low temperature in toluene in the presence of a small amount of zinc chloride as catalyst.[25]

(c) Functional Termination. The living CEVE polymerization was finally quenched after 6 h of reaction by adding a solution of lutidine and methanol to the polymerization media to convert the active chain termini into acetal ends, thus leading to poly(CEVE) of structure **4**. The polymer was then recovered by precipitation into methanol and characterized.

(d) Characterization of the Functional Poly(CEVE) Precursor. The NMR spectrum of a poly(CEVE) (**4**) prepared according to this procedure and the peak assignments are given in Figure 2. The polymer experimental molar mass measured by size exclusion chromatography (SEC) and the corresponding $\overline{DP}_n$ are indicated in Table 1. The latter are in good agreement with those obtained by NMR from the CEVE/acetal ratio, assuming two acetals per chain. However, as may be seen in Table 1, the experimental values are significantly lower than the corresponding theoretical polymer $\overline{DP}_n$ and molar masses, calculated assuming a unique and complete bifunctional initiation by the diiodo adduct of methylenebis(dioxolane). A typical SEC chromatogram of a poly(CEVE) is presented in Figure 3a. It shows the presence of a small peak tail in the low molar mass range, indicating the side formation of monofunctional poly(CEVE) chains, likely due to direct initiation by traces of HI which may come from the partial hydrolysis or decomposition of TMSI.

To prevent any side reaction of the monofunctional chains, during the ring-closure step, the poly(CEVE)s were fractionated by selective precipitation into methanol. The SEC chromatogram of the main recovered polymer fraction (~80%), corresponding to poly(CEVE) of structure **5**, is shown in Figure 3b. The dimensional characteristics of the fractionated linear precursors used for the cyclization are given in Table 2.

(e) Introduction of Styrenyl Head Groups. Poly(CEVE) **4** dissolved in CH_2Cl_2 was reacted with a weakly acidic HCl–methanol solution to regenerate the trimethylsilyl-protected hydroxy functions. The presence of methanol allowed us to keep unaffected the acetal ends despite the acid conditions. The NMR spectra of an α,α'-dihydroxy-ω,ω'-diacetal-poly(CEVE), structure **5**, is shown in Figure 4.

5 was then dissolved in dry tetrahydrofuran and reacted successively with sodium hydride and an excess of (iodomethyl)styrene (mixture of ortho and para isomers) to anchor the styrenyl group onto the poly(CEVE) hydroxy head functions by forming an ether linkage, thus leading to the polymer structure **6**. The NMR spectrum of **6** is given in Figure 5. The relative proton signal intensity between acetal ends (proton acetal singlet **e** located at 4.7 ppm (1H)) and styrenyl groups (aromatic protons centered at 7.3 ppm (4H), vinylic protons **i** at 5.25 and 5.7 ppm (2H), **h** centered at 6.6. ppm (1H), and oxymethylene protons **j** at 4.5 ppm (2H)) is in close agreement with the expected structure **6**. A good correlation is also observed between the molar masses and $\overline{DP}_n$ determined, on the one hand, from SEC curves and, on the other hand, from the NMR ratio monomers units/functional groups, assuming the presence of two acetal and two styrenyl groups on a poly(CEVE) chain; see data in Table 1.

The possibility to quantitatively and selectively activate the two polymer acetal ends in highly diluted solutions to promote their intramolecular reaction with the styrenyl groups and thus form bicyclic macromolecules was then examined.

II. Cyclization Procedure. Different cyclization routes based on pseudo-unimolecular coupling reactions have been recently explored for the synthesis of monocyclic polymers. These unimolecular reactions present the advantage to be very little dependent on the reagent concentration and therefore can be quite efficiently performed in the highly diluted conditions required to limit the intermolecular processes leading to polycondensates.

The general strategy utilized so far involves the activation of the linear precursor acetal ends by an electrophilic catalyst to form cation-like termini. The latter rapidly add onto the unsaturation of the styrenyl group attached at the other chain end while the adduct formed is not so reactive and does not interfere with the cyclization reaction.

Two distinct cyclization procedures have been already investigated.[28]: (i) an indirect activation route, first developed, which requires the conversion of the acetal end into an α-iodo ether function (this is quantitatively achieved by the addition of TMSI; the new function is activated by a strong Lewis acid, typically $SnCl_4$, under high dilution conditions to achieve cyclization); (ii) a "direct route" in which the acetal end is directly converted into a reactive carbocation, either in the

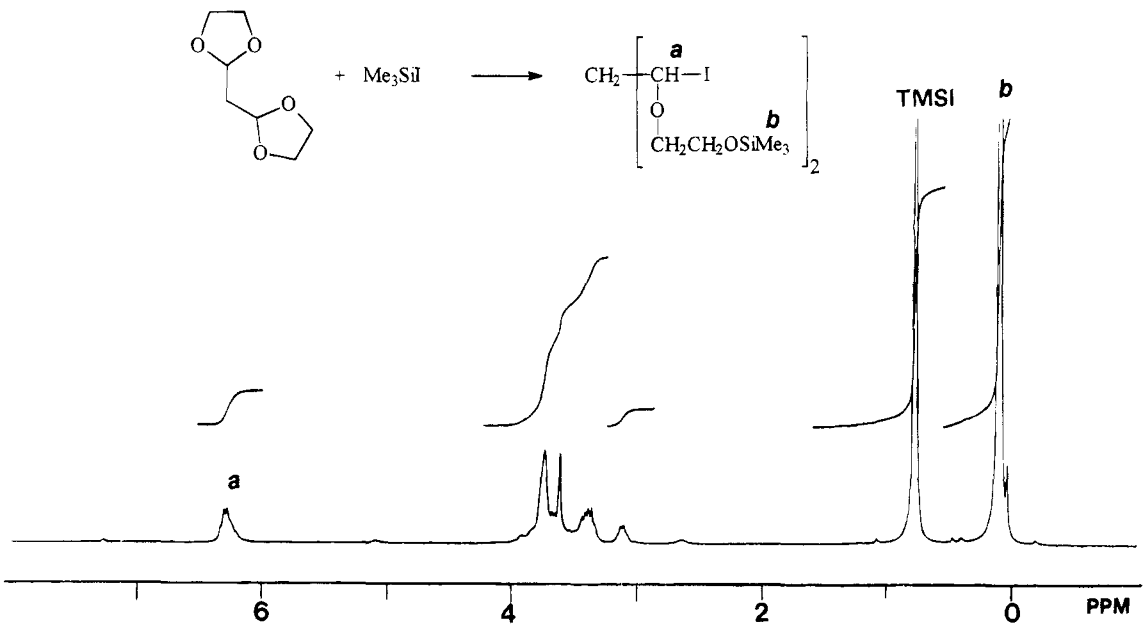


Figure 1. ^{1}H NMR (200 MHz) spectrum of the diiodo adduct of 1,1′-methylenebis(dioxolane) with trimethylsilane. An excess of TMSI was used. Solvent $CDCl_3$.

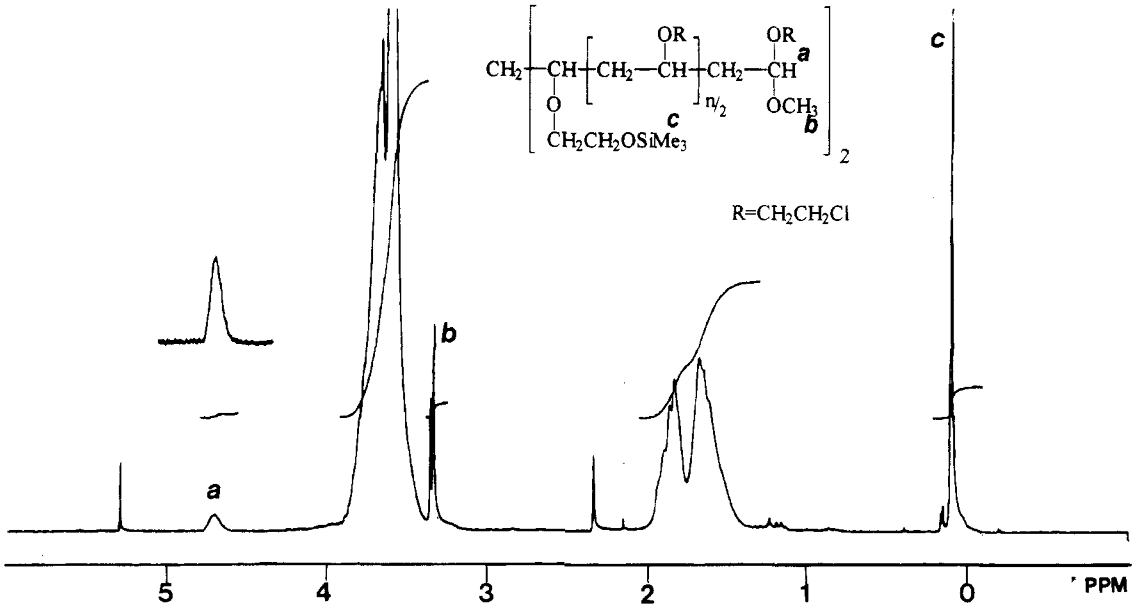


Figure 2. ^{1}H NMR (200 MHz) spectrum of α,α′-bis((trimethylsilyl)oxy)-ω,ω′-diacetal-poly(CEVE), $\overline{DP}_n = 25$. Solvent $CDCl_3$.

Table 1. Synthesis and Characterization of Linear α,α′-Dihydroxy-ω,ω′-diacetal-poly(CEVE)[a]

expt	MBDOX (10^{-3} M)	TMSI (10^{-3} M)	CEVE (M)	$\overline{DP}_{n,th}$[b]	$\bar{M}_{n,th}$[b]	$\bar{M}_{n,exp}$[c]	$\overline{DP}_{n,exp}$[d]	$\bar{M}_w/\bar{M}_n$
1	15.6	34.5	0.47	30.2	3440	2530	25	1.12
2	18.3	41.5	0.75	41	4590	3220	32	1.10
3	18.75	41.5	0.94	50.1	5560	4080	40	1.12
4	18.75	41.5	1.13	60.3	6646	6200	51	1.11

[a] Polymerizations were performed up to complete monomer conversion. MBDOX = 1,1′-methylenebis(dioxolane). [b] Assuming growth of one difunctional CEVE chain per MBDOX and complete polymerization. [c] Determined by SEC (polystyrene calibration). [d] Determined by proton NMR from the ratio (CEVE units/acetal end).

presence of strong Lewis acid and a protogenic compound or by the action of trimethylsilyl triflate (TMSOTf).

A recent study concerning the monocyclization of polystyrene suggests that the stability with time of the α-iodo ether termini is not so good and does not allow a slow addition of the activated polymer precursor. Accordingly, the cyclization should be preferably performed using the “direct route”.

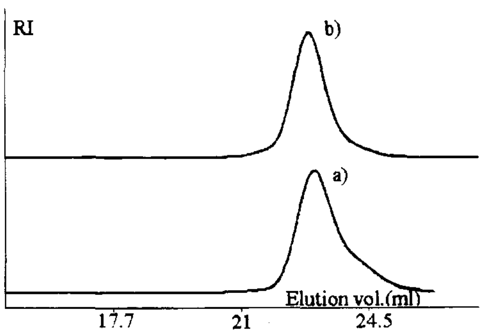


Figure 3. SEC chromatograms of α,α′-dihydroxy-ω,ω′-diacetal-poly(CEVE): (a) crude polymer ($\bar{M}_n = 2530$, linear polystyrene calibration); (b) after fractionation into methanol ($\bar{M}_n = 3620$, linear polystyrene calibration).

Table 2. Characteristics of Linear Poly(CEVE) Used as Chain Precursor and of the Corresponding Bicyclic Eight-Shaped Polymers

cycliz agent	sample no.	chain architecture	$\overline{DP}_n$	$\bar{M}_{n,exp}$[a]	M_p	$\bar{M}_w/\bar{M}_n$	$M_{p,bicycl}/M_{p,lin}$	estim yield (%)
TMSOTf	**1a**	lin	29	3620	3590	1.07		
		cycl		2930[b]	2920[b]	1.08	0.81	85
	2a	lin	32	3990	4200	1.06		
		cycl		3390[b]	3600[b]	1.15	0.85	60
$TiCl_4$	**2b**	lin	32	3990	4200	1.06		
		cycl		3380[b]	3500[b]	1.04	0.80	>90
	3a	lin	42	5050	5315	1.07		
		cycl		4320[b]	4330[b]	1.09	0.81	90
	4a	lin	53	6195	6170	1.09		
		cycl		5100[b]	4960[b]	1.08	0.80	>90

[a] Determined by SEC (polystyrene calibration). [b] Apparent molar masses determined by SEC on the basis of polystyrene calibration.

(a) Activation by $CF_3SO_3SiMe_3$(TMSOTf). The tetrafunctional poly(CEVE) precursor, **6** solubilized in dry 1,2-dichloroethane, was added dropwise under nitrogen to a large volume of ethylene dichloride containing a small amount of TMSOTf at −5°C. The solvent was carefully dried to prevent any hydrolysis of TMSOTf, since triflic acid can directly react with the styrenyl unsaturation. Assuming a fast coupling reaction, the instantaneous concentration of activated acetal polymer ends, i.e., one drop of polymer solution ($<5 \times 10^{-4}$ M) added to 1 L of solvent, may be estimated to be in the range 10^{-7}–10^{-8} M.

After complete addition of the polymer solution, the cyclization medium was neutralized by addition of methanol and triethylamine. The resulting polymer was finally recovered after partial solvent evaporation by precipitation into methanol and characterized. The corresponding results are discussed in a following section.

(b) Activation by Lewis Acids. Contrarily to TMSOTf, the presence of a small amount of a protogenic compound was found necessary to initiate the cleavage of acetals by Lewis acids and cleanly generate the corresponding carbocationic species. These protonic species were introduced by adding a small amount of water or alcohol to the solvent of the reaction or simply by the use of nonpurified methylene dichloride.[28] Addition of strong Lewis acids such as $SnCl_4$ or $TiCl_4$ to the chlorinated solvent containing traces of ROH or H_2O results in the partial hydrolysis of the Lewis acid with the formation of hydrogen chloride, which is believed to protonate one oxygen of the acetal function, leading thus to the transient formation of cationic polymer ends, able to react with the antagonist styrenyl function.

The experimental procedure used to achieve the cyclization of the polymer precursor is identical to the one described with TMSOTf.

(c) Characterization of the Bicyclized Poly(CEVE) (7). Characteristics of the linear poly(CEVE) precursor and the corresponding cyclized compounds obtained in the presence of either TMSOTf or a Lewis acid are collected in Table 2.

In the case of TMSOTf, as indicated by the change in the apparent polymer molar masses, M_p, determined by SEC, the cyclization proceeds to a large extent but is not quantitative. The formation of polycondensates and a slight broadening of the SEC peak (experiment n:2) attributed to the cyclized poly(CEVE) suggest that the dicyclization process is not clean and complete.

More reproducible and quantitative conversions are obtained by activation with $TiCl_4$. Further cyclization reactions were therefore performed by this procedure. As indicated in Table 2, an important shift of the apparent molar masses of the polymers, M_p values, is observed after the cyclization reaction, in agreement

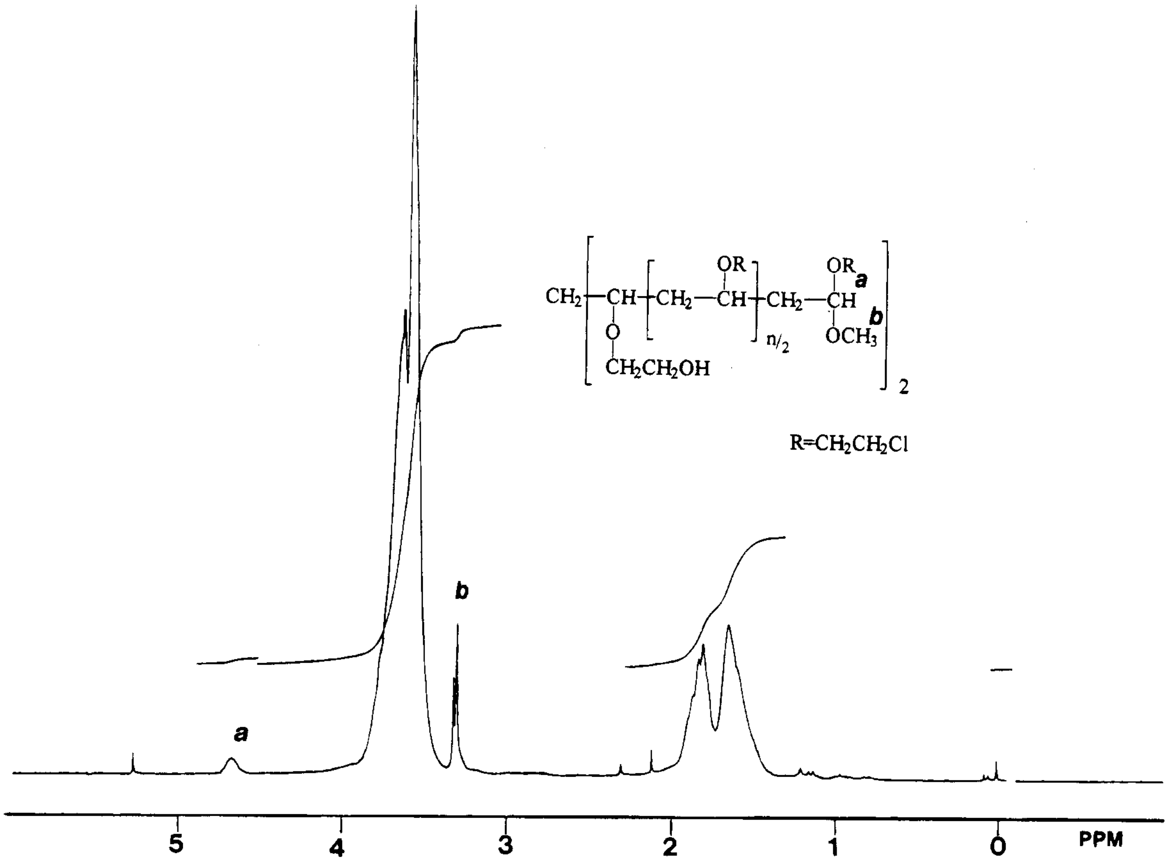


Figure 4. ^1H NMR (200 MHz) spectrum of α,α′-dihydroxy-ω,ω′-diacetal-poly(CEVE), $\overline{DP}_n = 29$. Solvent $CDCl_3$.

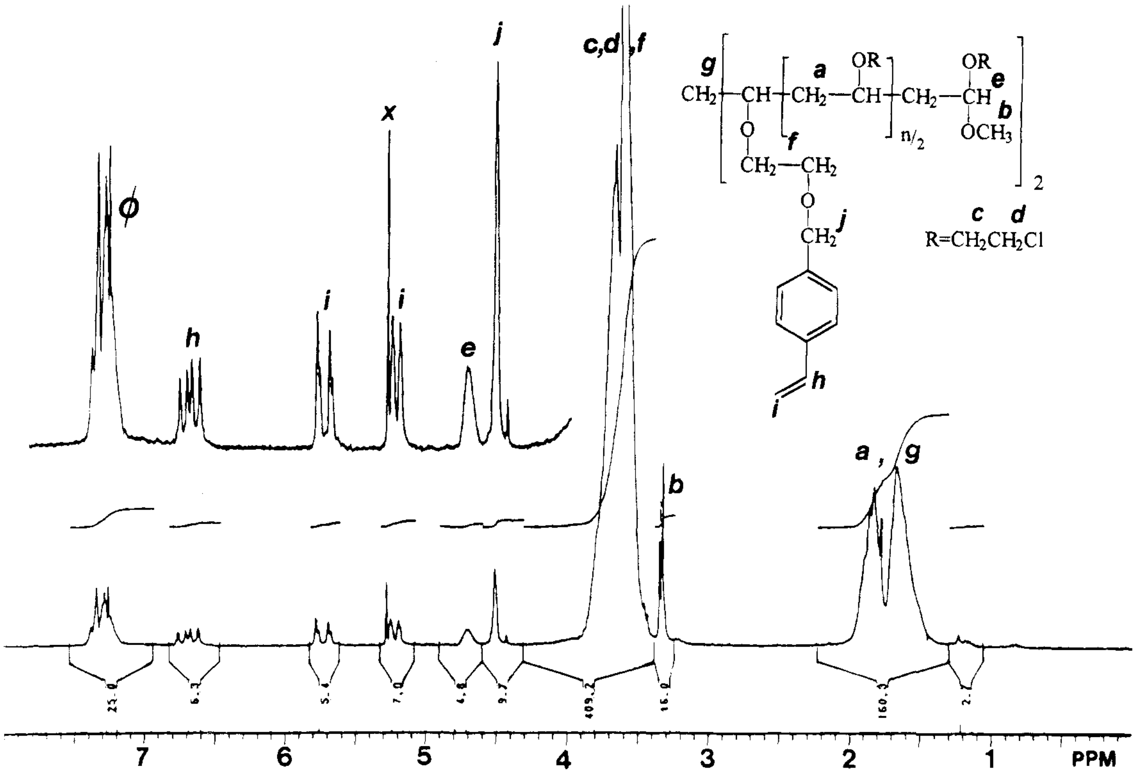


Figure 5. ^{1}H NMR (250 MHz) spectrum of α,α′-distyrenyl-ω,ω′-diacetal-poly(CEVE), $\overline{DP}_n = 17$. Solvent $CDCl_3$.

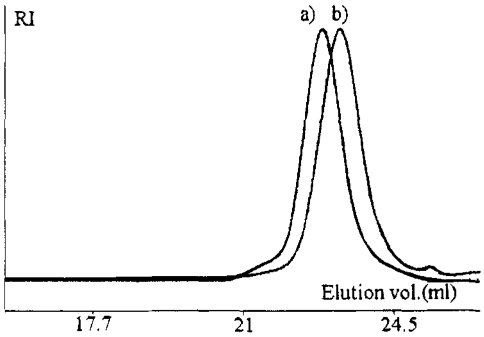


Figure 6. SEC chromatograms of α,α′-distyrenyl-ω,ω′-diacetyl-poly(CEVE): (a) linear precursor (M_p = 3590); and (b) corresponding polymer recovered after cyclization with $TiCl_4$ (M_p = 2920).

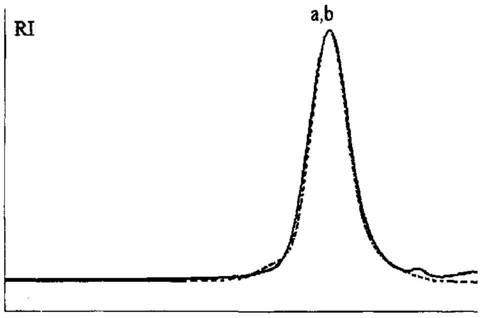


Figure 7. Fitting of SEC chromatograms of (a) the linear precursor (M_p = 3590) and (b) the corresponding cyclized polymer (M_p = 2920) (see Figure 6).

with the expected reduction of the hydrodynamic volume of the cyclized products. Characteristic SEC chromatograms of a linear poly(CEVE) and the corresponding cyclized polymer are shown in Figure 6. The SEC trace of the cyclized poly(CEVE) indicates that the formation of polycondensates is negligible. Besides, the superposition of the linear and cyclized polymer SEC traces (Figure 7) confirms that no broadening of the molar mass distribution occurs during the cyclization reaction. Since the linear polymer precursor, the monocyclic polymer with two pendant arms, which may result from an incomplete cyclization reaction, and the expected bicyclic polymers should all have different elution volumes, the narrow molar mass distribution of the recovered polymers strongly supports the clean formation of bicyclic macromolecules. This conclusion is also supported by the complete disappearance of the acetal and styrenyl polymer ends of the linear precursor, as may be seen in the NMR spectra of the cyclized polymer (Figure 8). Accordingly, yields into bicylic poly(CEVE)s can be estimated to be higher than 90% for cyclization performed in the presence of $TiCl_4$.

The experimental ⟨G⟩ values for the bicyclic poly(CEVE)s, obtained from the ratio $M_{p,bicycl}/M_{p,lin}$, are also indicated in Table 2. They are close to 0.8, a value in between those found for monocyclic poly(CEVE) (⟨G⟩ = 0.83–0.85)[25] and tricyclic poly(CEVE) (⟨G⟩ = 0.75–0.80).[30] These last two data need, however, to be reconfirmed since the procedures used at that time for the synthesis of mono- and tricyclic poly(CEVE) were not fully controlled and the presence of linear polymer impurities cannot be completely excluded. Besides, it is interesting to note that the ⟨G⟩ values of bicyclic poly(CEVE) are very close to those observed for monocyclic polystyrenes.[9,15,28]

These results might suggest that the hydrodynamic volume of bicyclic eight-shaped polymers is not noticeably lower than that of a monocyclic polymer of the same molecular weight.

Finally, a series of experiments was performed to investigate the possible complexation of organic molecules, such as dyes (pyrocatechol violet) and hemin, by the bicyclic poly(CEVE), as already found in the case of tricyclic poly(CEVE)s.[31] No complexation could be observed with the different compounds despite the fact

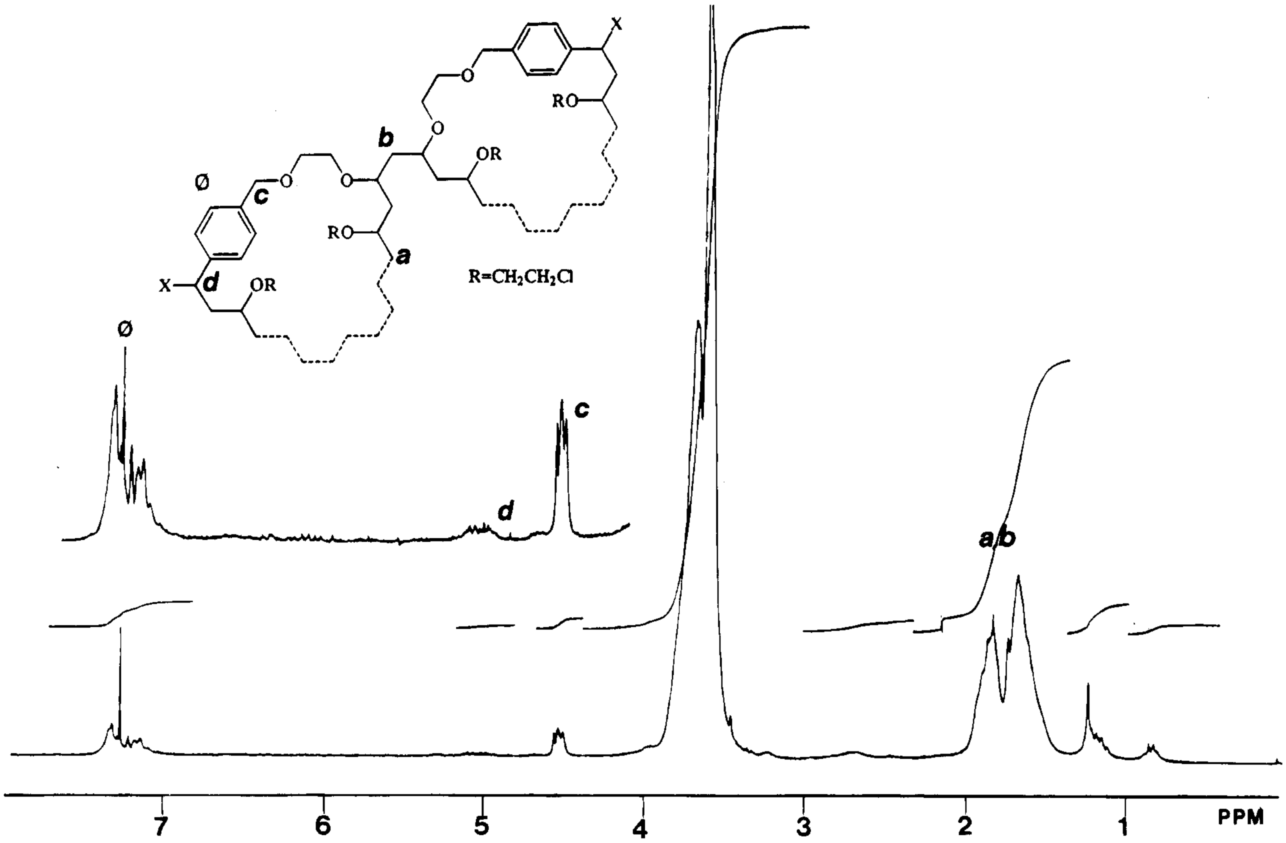


Figure 8. ^{1}H NMR (200 MHz) spectrum of a bicyclic poly(CEVE), $\overline{DP}_n = 29$. Solvent $CDCl_3$.

that they show a strong affinity to the tricyclic polymers, suggesting that the (so-formed) macrobicyclic structure is not appropriate for the development of such interactions.

In conclusion, the synthesis of new bicyclic eight-shaped poly(CEVE)s of controlled dimensions has been achieved almost selectively and quantitatively using cyclization procedures based on a unimolecular coupling reaction, thus demonstrating the efficiency of this approach for the synthesis of ring-shaped polymers. Further characterization of the structure and the properties of these macrobicyclic polymers is, however, needed. These studies are in progress. Besides, the synthesis of new macrocyclic and plurimacrocyclic polymers by this approach is under investigation and will be reported in the near future.

Experimental Section

Materials. 1,1,3,3-Tetramethoxypropane(Aldrich, purity >99%), $TiCl_4$ (Aldrich, purity >99.9%), and Me_3SiI Aldrich, purity >99%) were used as received. CEVE was washed with a 10% aqueous sodium hydroxide solution and water and distilled twice over calcium hydride before use. $ZnCl_2$ (Aldrich, purity >99%) was dried under vacuum and sublimed. Ether and toluene were purified by the usual methods and dried over sodium–benzophenone.

Synthesis of 1,1′-Methylenebis(dioxolane) (1). 1,1,3,3-Tetramethoxypropane (10 g (0.061 mol)) and 8.3 g (0.0134 mol) of ethylene glycol are heated at 80 °C for 1 h in the presence of 1 mL of HCl (1 N). After cooling to room temperature, 1,1′-methylenebis(dioxolane) is extracted with pentane and recrystallized twice at low temperature.

Synthesis of the α,α′-Dihydroxy-ω,ω′-diacetalpoly(CEVE) (5). To 0.2 g of 1 (0.00125 mol) solubilized in 50 mL of anhydrous toluene is added under nitrogen 2.75×10^{-3} mol of pure TMSI. After standing at 0 °C for about 30 min, the solution is cooled to −35 °C, and then CEVE (0.05 mol for a $\overline{DP}_n$ of 2 × 20(and $ZnCl_2$ (1 mL of a 10^{-1} M ether solution) are successively introduced. After about 6 h, the polymerization is stopped by adding 6 mL of a 1 M solution of lutidine into methanol to convert the polymer ends into acetals.

The poly(CEVE) was recovered by solvent evaporation, redissolved in methylene dichloride, and washed several times with 500 mL of an aqueous HCl solution (1 N) to deprotect the polymer hydroxy groups.

Fractionation of the poly(CEVE) to eliminate the low molar mass fraction corresponding to monofunctional chains is achieved by adding methanol dropwise to the polymer solution until the precipitation of the high molar mass fraction is observed.

Anchoring of the Styrenyl Groups. α,α′-Dihydroxy-ω,ω-diacetal-poly(CEVE) (5 g) is solubilized into 100 mL of anhydrous tetrahydrofuran under nitrogen, and 0.1 g of sodium hydride (4.2×10^{-3} mol) is added. After standing for 1 h, 1 g of (iodomethyl)styrene (mixture of ortho and para isomers) is introduced, and the mixture is stirred for 18 h at room temperature. The polymer solution is then washed with water and precipitated several times into methanol. The quantitative grafting of the styrenyl groups was controlled by NMR. When the reaction was incomplete, the anchoring procedure was repeated.

Cyclization of the Poly(CEVE). Poly(CEVE) precursor (2 g) solubilized in 10 mL of methylene dichloride is added dropwise in about 6 h into 1 L of methylene dichloride containing the cyclization catalyst. In the case of experiments performed with trimethylsilyl triflate, the solvent, 1,2-dichloroethane, was carefully dried over calcium hydride. For experiments performed with

$TiCl_4$, the solvent was used as received (methylene dichloride, stabilized with 0.3% of ethanol). Pure $TiCl_4$ was introduced in large excess, about 30 times, with respect to the acetal ends.

When the addition of the precursor solution was complete, the reacting medium was neutralized with a solution of methanol and ammonia. The salts were eliminated by filtration. The polymer solution was washed and the poly(CEVE) recovered by precipitation into methanol.

Polymer Characterization. The proton NMR spectra of the initiator and the different polymers were recorded in an AC 200 MHz FT Brüker spectrometer. The polymer molecular weights (linear precursors) and MWD's were determined in THF by SEC using a Varian chromatograph equipped with RI and UV detectors and fitted with three TSK columns (G2000, G3000, G4000 HXL), calibrated using polystyrene standards.

Investigation of the complexation capacities of bicyclic poly(CEVE) toward pyrocatechol and hemin was performed as previously described.[31] Pyrocathechol and hemin solubilized into methanol were tentatively extracted with a solution of bicyclic compound in methylene dichloride, a nonsolvent of the two organic compounds. Their concentration in methylene dichloride was then determined by UV–visible spectroscopy.

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References and Notes

(1) Hild, G.; Kohler, H.; Rempp, P. *Eur. Polym. J.* **1980**, *16*, 525.

(2) Geiser, G.; Hoecker, H. *Polym. Bull.* **1980**, *2*, 591; *Macromolecules* **1980**, *13*, 653.

(3) Vollmert, B.; Huang, J. X. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 467.

(4) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.

(5) Hild, G.; Strazielle, C.; Rempp, P. *Eur. Polym. J.* **1983**, *19*, 721.

(6) Roovers, J. *Macromolecules* **1985**, *18*, 1361.

(7) Lutz, P.; McKenna, G. B.; Rempp, P.; Strazielle, C. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 599.

(8) Semlyen, J. A., Ed. *Cyclic Polymers*; Elsevier Applied Science, London, 1986.

(9) Lutz, P.; Strazielle, C.; Rempp, P. *Recent Advances in Anionic Polymerization*; Hogen-Esch, T. E., Smid, J., Eds.; Elsevier Science Publishers: Amsterdam, 1987; p 403.

(10) McKenna, G. B.; Hadziioannou, G.; Lutz, P.; Hild, G.; Strazielle, C.; Straupe, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 1851.

(11) Quirk, R. P.; Ma, J. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 10.

(12) McKenna, G. B.; Hostetter, B. J.; Hadjichristidis, N.; Fetters, L. J.; Plazek, D. J. *Macromolecules* **1989**, *22*, 1834.

(13) Penczek, S.; Slomkowski, S. *Comprehensive Polymer Science*; Pergamon Press: Oxford, 1989; Vol. 3, p 725.

(14) Liu, X.; Chen, D.; He, Z.; Zhang, H.; Hu, H. *Polym. Commun.* **1991**, *32* (4), 123.

(15) Sundurarajan, J.; Hogen-Esch, T. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)* **1991**, *32* (3), 604.

(16) Roovers, J.; Toporowski, P. M. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *2*, 1251.

(17) Hogen-Esch, T. E.; Sundurarajan, J.; Toreki, W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym.* Sci.) **1988**, *29* (2), 17.

(18) Antonietti, M.; Fölsch, K. J. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 423.

(19) Hogen-Esch, T. E.; Sundurarajan, J.; Toreki, W. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 23.

(20) El Madani, A.; Favier, J. C.; Hémery, P.; Sigwalt, P. *Polym. Int.* **1992**, *27*, 353.

(21) Clarson, S. J.; Semlyen, J. A.; *Siloxane Polymers*; Polymer Science and Technology Series; Mark, J. E., Ed.; Prentice-Hall: Englewood Cliffs, NJ, 1993; Chapter III.

(22) Yin, R.; Hogen-Esch, T. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)* **1992**, *33* (1), 239; *Macromolecules* **1993**, *26*, 6952.

(23) Ma, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)* **1993**, *34* (2), 626.

(24) Gan, Y. D.; Zöller, J.; Yin, R.; Hogen-Esch, T. E. *Macromol. Symp.* **1994**, *77*, 93.

(25) Schappacher, M.; Deffieux, A. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 447.

(26) Deffieux, A.; Schappacher, M.; Rique-Lurbet, L. *Polymer* **1994**, *35*, 21, 4562.

(27) Rique-Lurbet, L.; Schappacher, M.; Deffieux, A. *Macromolecules* **1994**, *27*, 6318.

(28) Deffieux, A.; Schappacher, M.; Rique-Lurbet, L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2) 494.

(29) Hémery, P.; Boutillier, J. M.; El Madani, A.; Favier, J. C., Sigwalt, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 478.

(30) Schappacher, M.; Deffieux, A. *Macromolecules* **1992**, *25*, 6744.

(31) Schappacher, M.; Deffieux, A. *Polym. Adv. Technol.*, in press.

(32) Van Merveine, D.; Haucourt, N.; Goethals, E. J. *Polym. Bull.* **1990**, *23*, 185.

(33) Goethals, E. J.; Haucourt, N.; Li-bing Pen, *Macromol. Symp.* **1984**, *85*, 97.

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