Synthesis and Characterization of Ring-Shaped Polystyrenes

Bénédicte Lepoittevin,[†] Marie-Anne Dourges,[†] Michèle Masure,[†] Patrick Hemery,*[,†] Katia Baran,[‡] and Henri Cramail[‡]

Laboratoire de Chimie des Polymères, Unité Mixte associée au CNRS, UMR 7610, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France; and Laboratoire de Chimie des Polymères Organiques, UMR 5629, ENSCPB-CNRS, Université Bordeaux-1, Avenue Pey Berland, BP 108, 33402 Talence Cedex, France

Received January 13, 2000; Revised Manuscript Received June 28, 2000

ABSTRACT: Macrocyclic polystyrenes were prepared by coupling a two-ended living precursor dianions with 1,3-bis(1-phenylethylenyl)benzene (DDPE). Experiments were performed in a drybox apparatus, and macrocycles were obtained with a yield ranged between 40 and 55%. Simultaneously, besides the expected cyclic polymer, polycondensates (linear and cyclic) were formed. Thus, macrocyclic products were separated from the residual linear precursor and linear polycondensates byproducts by preparative high performance liquid chromatography at the exclusion−adsorption transition point. Isolation of highly pure cyclic polystyrenes (of different sizes) was carried out. Information on the chemical structure of the linear and cyclic polystyrenes were obtained by matrix-assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectrometry, showing a good agreement with the expected structures. In addition, viscometry measurements by SEC (viscometry detector) showed that the ratio $g' = [\eta]_C/[\eta]_L$ is equal to 0.67 in a good solvent and confirmed the high efficiency of the preparative liquid chromatographic separation.

Introduction

Cyclic macromolecules are of great interest in the investigation of the influence of cyclization on their solution, melt, and solid-state properties.[1−3] The earlier studies on cyclic macromolecules are essentially theoretical,[4−6] describing the effect of cyclization on the dimensions of macromolecules and predicting the solution behavior. The first synthetic method produces cyclic polymers by ring-chain equilibria based on backbiting reactions.[7−8] Such reactions, studied in the case of poly(dimethylsiloxane)s, lead to the preparation, isolation, and characterization of well-defined cyclic products. However, this method has two limitations: the domain of molar masses is less than 30 000 g·mol^{-1}, and the linear precursor of the same molar mass cannot be obtained in the same synthesis. The second method to obtain macrocyclic polymers uses anionic polymerization techniques: a bifunctional living precursor polymer reacts at very low concentration with a stoichiometric amount of a bifunctional electrophile (dihalogeno or diethylenic compound). The advantage of this method is that cyclic polymers can be prepared with molar masses up to 400 000 g·mol^{-1} and with a narrow distribution; moreover, the precursor and the cyclic product of the same molar mass can be obtained during the same synthesis. Cyclic polystyrenes,[9−14] poly(2-vinylpyridine)s,[15−16] polydienes,[17−19] and copolymers[20−22] have been prepared by this method. A different approach based on the cyclization of an α,ω-heterodifunctional precursor via a pseudo-unimolecular reaction was recently investigated[23,24] for the preparation of cyclic polystyrenes and of poly(vinyl ether)s. It involves the reaction, after appropriate activation, of one of the active ends of the precursor with the other end-function of the same polymer chain.

Characterization of the ring structures is achieved by different techniques such as size exclusion chromatography (preferably in association with small-angle neutron scattering or quasi elastic light scattering[25]) and viscometry. The purity of theses ring polymers (lack of contamination by linear polymer) is not known with accuracy since analytical techniques were limited. Unfortunately, the presence of small amounts of linear polymer can crucially affect the properties (such as melt viscosity[26]) of ring polymers. Recently, two new techniques have been developed to characterize and check the purity of ring polymers simultaneously: matrix-assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectrometry and liquid chromatography at the exclusion−adsorption transition point (LC PEAT). Combination of these techniques can also be used for the characterization of ring structures.

MALDI−TOF mass spectrometry, introduced by Karas and Hillenkamp,[27] is a powerful new technique able to provide the molar mass, composition, and functionality of polymers. The molar mass distribution data of narrowly distributed polymers may be provided with good accuracy up to molar mass values of about 200 000 g·mol^{-1} [28]. Moreover MALDI−TOF mass spectrometry can characterize end-group functionalities of low molar mass polymers (<15 000 g·mol^{-1}) exhibiting a narrow distribution. Analyses of polystyrene were previously reported,[29,30] and chemical structures of macrocyclic products have already been determined.[31]

Liquid chromatography at the exclusion−adsorption transition point (LC PEAT) allows the separation of polymers according to their heterogeneity (polymers with functional groups, block copolymers, grafted polymers) by operating at the transition point of size exclusion and adsorption modes of liquid chromatography.[32−34] At their critical point of adsorption, the linear macromolecules elute at the same time whatever their molar mass allowing for the separation of cyclic polymers from their linear analogues.[35,36]

[†] Université Pierre et Marie Curie.
[‡] Université Bordeaux-1.

10.1021/ma000059q CCC: $19.00
Published on Web 10/04/2000

Cyclization reaction using a diethylenic compound (i.e., DDPE) leads to a reactive cyclic compound possessing two active centers. In a second step, products with more complex architecture containing cyclic parts (cyclic-based networks, multicyclic products) could be prepared by intermolecular reaction between functionalized macrocycles.

In this work, macrocycles were prepared by the reaction of linear polystyrene having two living ends with DDPE as a coupling agent.[13,37] The intramolecular reaction being in competition with intermolecular reaction, polycondensates of higher molar mass are simultaneously formed, leading to a mixture of linear and cyclic structures that are not differentiated well by SEC measurements on the crude material. Cyclic and linear structures were separated by preparative LC PEAT in order to obtain a pure fraction of cycles. Confirmation of cyclization was obtained by analysis of the chemical structure by MALDI−TOF mass spectrometry and by viscosity measurements.

Experimental Section

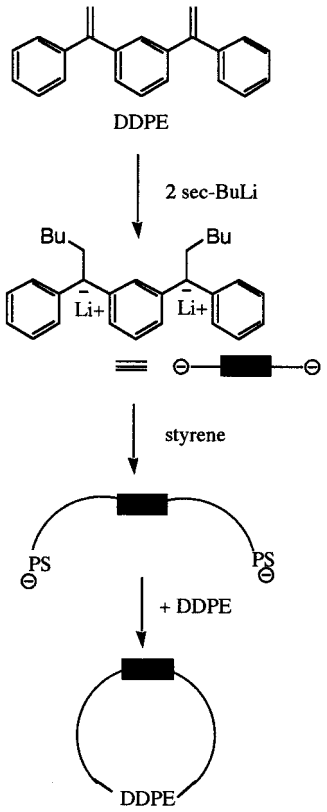
Materials. Hexane (Prolabo, 99% RP Normapur), benzene (Acros, 99%), tetrahydrofuran (THF) stabilized with 2,6-di-*tert*-butyl-4-methylphenol (SDS, 99.7%), and styrene (Aldrich, 99%) were dried and distilled over sodium before use. 1,3-Bis(1-phenylethylenyl)benzene (DDPE) was synthesized and purified using the procedure of Schulz and Höcker.[38] *sec*-Butyllithium (1.3 mol·L^{-1} solution in hexane, Aldrich) was used as received.

Polymerization and Cyclization Reactions. Experiments were performed in a drybox. In a typical procedure, the dilithium initiator was prepared in benzene at room temperature for 16 h by the addition reaction of 2 equiv of *sec*-butyllithium (2.7×10^{-4} mol, 20 mL of a solution of 1.35×10^{-2} mol·L^{-1}) with 1 equiv of DDPE (1.35×10^{-4} mol, 3.4 mL of a solution of 4×10^{-2} mol·L^{-1}). The styrene polymerization was carried out during 1 h by reaction of the dilithium initiator (1.73×10^{-4} mol of active centers, 15 mL of the dilithium initiator solution) in the presence of 25 equiv of tetrahydrofuran (4.3×10^{-3} mol, 0.35 mL) with styrene (6×10^{-3} mol, 0.7 mL, $DP_n = 70$) at room temperature. The concentration of active sites (addition of BuLi on DDPE and polymerization of styrene) was measured by UV spectrometry. Cyclization reaction was performed at room temperature during 3 h by introducing a stoichiometric amount of DDPE (2.7×10^{-5} mol, 0.66 mL of a solution of 4×10^{-2} mol·L^{-1}) into the living polymer solution (5.35×10^{-5} mol, 5 mL of the living polymer solution) after dilution with benzene (36 mL) and hexane (36 mL) to reach a concentration in active centers of $\approx 7 \times 10^{-4}$ mol·L^{-1}. The polymer was deactivated by addition of methanol (0.5 mL), precipitated in methanol, and dried to yield 0.19 g of polystyrene as a white solid (53% of cyclic polystyrene $M_n = 6900$ g·mol^{-1}, pdi = 1.12, and 47% of polycondensates).

Size Exclusion Chromatography (SEC) (Refractive Index and Ultraviolet Detectors). SEC was performed using a Waters apparatus working at room temperature with tetrahydrofuran eluent at a flow rate of 1 mL·min^{-1} and equipped with four PL-gel 10 μ columns (100, 500, 10^3, and 10^4 Å). Differential refractive index (LDC Analytical) and UV (Waters 484 tunable Absorbance detector) detectors were used, and molar masses were determined from a calibration curve based on linear polystyrene standards.

Size Exclusion Chromatography (Refractive Index and Viscometry Detectors). SEC was performed using a Waters apparatus working at 30 °C with tetrahydrofuran eluent at a flow rate of 1 mL·min^{-1} and equipped with three columns Shodex (exclusion limit: 2×10^4, 4×10^5, and 4×10^6 g·mol^{-1}). A differential refractive index (Viscotek) and viscometry (Viscotek DM 400) detectors were used, and molar masses were determined from a calibration curve based on linear polystyrene standards.

Scheme 1. Reaction Pathway for the Synthesis of Cyclic Polystyrenes



HPLC Equipment. LC PEAT experiments were carried out on a modular HPLC system composed of a VARIAN model pump. An Ultra-violet Spectrophotometric detector working at 261 nm was used.

Analytical Chromatography. The flow rate was 1 mL·min^{-1} at 25 °C. A Nucleosil silica column, dimension 250 × 4.6 mm, filled with particles of 5 μm size and porosity of 100 Å, was used. The eluent was THF/hexane (47.9/52.1 wt %)

Preparative Chromatography. The flow rate was 15 mL·min^{-1} at 25 °C. A Kromasil silica column, dimension 250 × 20 mm, was used, filled with particles of 5 μm size and porosity of 100 Å. The eluent was THF/hexane (50.5/49.5 wt %).

MALDI−TOF Mass Spectrometry. MALDI−TOF mass spectrometry was performed using a PerSeptive Biosystems Voyager Elite time-of-flight mass spectrometer equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. The MALDI mass spectra represent averages over 256 laser shots. This instrument operated at an accelerating potential of 20 kV in both linear and reflector modes.

The polymer solutions (2−5 g·L^{-1}) were prepared in THF. The matrix 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol) was dissolved in THF (10 g·L^{-1}). The polymer solution (10 μL) was mixed with 50 μL of the matrix solution, and 10 μL of a silver trifluoroacetate solution (2 g·L^{-1} in THF) was added to favor ionization by cation attachment. A 1 μL portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Internal standards (peptides or porphyrin derivatives) were used to calibrate the mass scale using the two-point calibration software 3.07.1 from PerSeptive Biosystems.

Results and Discussion

Synthesis and SEC Characterization. The macrocyclic polystyrenes were synthesized by living anionic polymerization according to the general pathway given in Scheme 1. The dilithium initiator was formed by

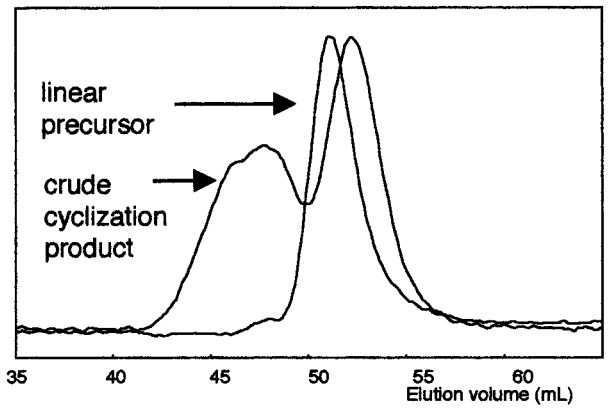


Figure 1. SEC chromatograms of linear precursor and crude cyclization product (sample PS2, Table 1): mobile phase, THF; detection, refractive index.

Table 1. SEC Data for Linear (L) and Macrocyclic (C) Polystyrenes

samples	M_{nL}	M_w/M_{nL}	M_{pL}[a]	M_{pC}[a]	$\langle G \rangle$[b]	yield, %[c]
PS1	5600	1.19	7000	4800	0.70	49
PS2	6900	1.12	8600	6440	0.75	53
PS3	10500	1.14	13800	10500	0.75	46
PS4	13700	1.12	15500	11800	0.76	40

[a] SEC peak molar mass for linear precursor L and crude cyclization product C. [b] $\langle G \rangle = M_{pC}/M_{pL}$. [c] Cyclization yield of coupling reaction estimated from SEC chromatogram of crude cyclic polymer.

addition reaction of 2 mol of *sec*-butyllithium on 1 mol of DDPE.

Polymerizations of styrene were carried out in the presence of THF as additive to obtain a sufficiently narrow molar mass distribution ($M_w/M_n < 1.2$). In these conditions, the stability of the active sites was satisfactory but the chromatogram is not perfectly symmetrical indicating a relatively slow initiation. Cyclization reaction was performed by linking the dilithium polystyrene with the coupling agent (DDPE) after dilution of the solution in a mixture benzene/hexane (50/50 vol %) with a relatively concentrated solution (7×10^{-4} mol·L^{-1} in active centers). The presence of a nonsolvent (hexane) reduces the expansion of the polymer chain and facilitates slightly intramolecular coupling as was already shown by several authors.[9,15] The presence of a nonsolvent may cause the formation of knotted rings,[39,40] but was not observed in these conditions (dilution). The crude product of cyclization and the linear precursor were first characterized by SEC (Figure 1, sample PS2 in Table 1). The SEC chromatogram of the crude cyclization product shows two peaks. The peak at an elution volume slightly higher than that of the precursor polystyrene corresponds to the expected macrocycles. The second peak at lower elution volume corresponds to polycondensate byproducts, the intramolecular cyclization being in competition with intermolecular reactions.

The hydrodynamic volume[9−24] of a cyclic polymer is lower than that of a linear one having an identical molar mass. As molar mass obtained by SEC is derived from their hydrodynamic volume, one should expect to see an apparent decrease in molar mass upon cyclization. Table 1 summarizes the characterization results of linear polystyrenes precursors of different molar mass and of the products obtained by cyclization; it illustrates the difference in elution volume by the ratio of the apparent peak molar mass (that could be slightly different after separation of the species) for each linear precursor/cycle pair ($\langle G \rangle$). These results show a good agreement between the experimental molar masses and the theoretical values. As expected, the apparent molar mass of the macrocycles are lower than their linear precursors, and $\langle G \rangle$ varies between 0.7 and 0.78 for all samples. Other authors[9,12,48] have measured this ratio for polystyrene in good solvents and found values ranging between 0.71 and 0.81, in good agreement with our results.

The fraction of polycondensates increases from 45 to 60% with an increasing molar mass (the exception for sample PS1 is in the range of the experimental accuracy) confirming the fact that the increase of molar mass disturbs intramolecular reaction.

Cyclic polymers elute later than linear polymers but the difference in the elution volume is too small to determine the residual linear fraction in the cyclization products. Contamination by uncyclized chains having reacted with DDPE (monoaddition) was pointed out by SEC (UV detector). The absorbance of the diphenylethylene being larger than that of the benzene ring at 254 nm, the peak intensity increases after monoaddition with DDPE.

In this case, experiments were carried out using simplified conditions compared to the usual drastic conditions (high vacuum techniques and sealed apparatus). The syntheses were performed in a drybox apparatus and the concentration of active centers during the cyclization is relatively high (7×10^{-4} mol·L^{-1} compared to the 10^{-5}−10^{-6} mol·L^{-1} usually attained) and leads however to a good yield (40−60%) in macrocycles. Using a diethylenic compound as coupling agent is a favorable factor for cyclization reaction[18] and gives a better yield than dihalogeno coupling agents. Previous studies showed that the rate of addition on the second double bond was several times higher than that for the first one.[41,42] Moreover, as polystyryllithium is aggregated in a polar solvent, it was postulated[18] that cross-associated cyclic species are formed and can favored cyclization reaction. These favorable conditions allow to obtain crude cyclization product in sufficient amount (150−300 mg) for purification by preparative liquid chromatography before further characterizations.

The SEC chromatogram (Figure 1) shows the presence of polycondensates of twice or more the expected molar mass but does not indicate the nature (cyclic or linear) of these byproducts. Separation of cyclic constituents was achieved by LC PEAT in order to obtain a pure fraction of cyclic material.

Liquid Chromatography Characterization and Macrocycle Isolation. As was already outlined in the Introduction, liquid chromatography at the exclusion−adsorption transition point (LC PEAT) is well-suited for separation of cyclic polymers from their linear analogues. The critical point of adsorption of standards polystyrene was previously determined[43] on a silica stationary phase with a mixture of THF and *n*-hexane as eluent. Several polystyrene standards exhibiting different molar masses were analyzed in eluents of different compositions. At high concentration of THF (>47 wt %), the retention time decreases with an increase of the molar masses corresponding to the size exclusion mode. At THF concentration <47 wt %, the adsorption mode is operating and the retention time of polystyrene increases with the molar mass. At the eluent composition THF/hexane = 47/53 wt %, the

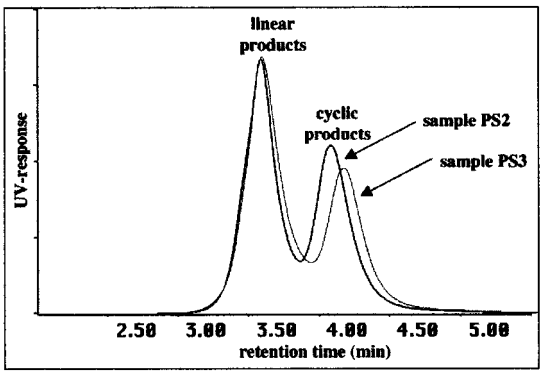


Figure 2. Critical chromatograms of samples PS2 and PS3: stationary phase, Nucleosil silica; mobile phase, THF/hexane (47.9/52.1 wt %); detection, UV 261 nm.

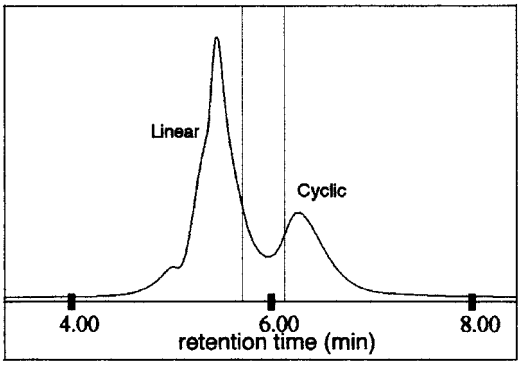


Figure 3. Preparative critical chromatogram of sample PS2: stationary phase, silica; mobile phase, THF/hexane (50.5/49.5 wt %); detection, UV 261 nm.

retention time does not change with molar mass and the separation is accomplished exclusively with the chemical or topological heterogeneity. The critical conditions were verified for linear precursors of different molar masses, showing good reproducibility of the conditions.

The elution behavior of two linear precursors and cyclization products is reported in Figure 2. The linear samples elute at about 3.54 min. For the crude cyclization product, two separated elution region can be observed: residual linear products elute at 3.54, 3.57, and 3.58 min; cyclic products elute at higher retention times, 4.01, 4.06, and 4.15 min for molar masses of 5600, 6900 and 10 500 g·mol^{-1} respectively. The elution time of cycles is higher than that of linear products in agreement with theory.[44] The retention time of cycles increases slightly with molar mass indicating that these products behave in adsorption mode.

Then, the crude cyclization product (200 mg) was purified by preparative liquid chromatography in order to isolate macrocycles from linear products (Figure 3). The two fractions obtained were analyzed by SEC and MALDI−TOF in order to achieve a complete description of the composition of the crude cyclization product.

The two fractions (cyclic and linear products) were first analyzed by SEC. The SEC chromatograms are given in Figure 4, and the SEC data for the fractionated polymers are listed in Table 2. Concerning the linear product fraction, the chromatogram shows several peaks. A small peak at higher elution volume indicates the presence of residual linear precursor; the large peak at low elution volume corresponds to linear polycondensates of the precursor (dimer, trimer, ...).

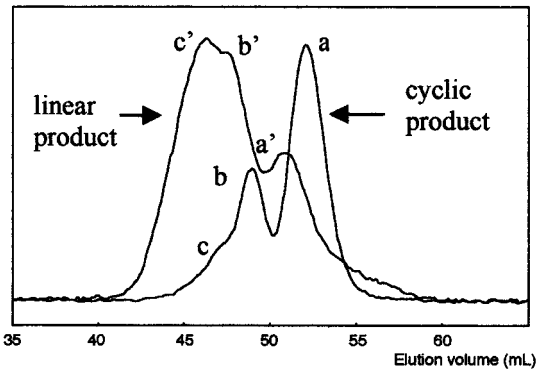


Figure 4. SEC chromatograms of fractions of linear and cyclic products obtained by preparative liquid chromatography (sample PS2): mobile phase, THF; detection, refractive index.

Table 2. SEC Data for Linear and Cyclic Products Obtained by Preparative Liquid Chromatography (Sample PS2)

products	M_{peak}	SEC attribution
monomeric cycle	6500	cycles fraction a
linear precursor	8400	linears fraction a′
dimeric cycle	13400	cycles fraction b
linear dimer	18800	linears fraction b′
trimeric cycle	19700	cycles fraction c
linear trimer	26600	linears fraction c′

Concerning the fraction of cyclic products, an interesting feature of the chromatogram is that, in addition to the major peak corresponding to the expected cycle, small peaks are obtained. These peaks indicate the presence of dimeric and trimeric cycles in the mixture in small proportions (≅35% estimated from SEC chromatogram), the presence of small amounts of dimeric cycles was already supposed in the literature[12] but was never demonstrated.

Several authors have already used LC PEAT for the separation of linear and cyclic[35,36] products according both to their architecture and functionality. In the present case, liquid chromatography separates polymers according only to their architecture, the linear precursor and the cyclic product presenting few differences in chemical composition (the same product (DDPE) was used as initiator and as coupling agent).

As was already shown for the monomeric cycle, the chromatogram shows a difference between the elution volume of each pair linear/cyclic dimer and linear/cyclic trimer. As expected the cyclic dimer and trimer have a smaller hydrodynamic volume than the linear dimer and trimer. The peak molar mass of the polycondensates products is obtained by deconvolution of the chromatograms. The ratio ⟨G⟩ for dimeric and trimeric products is on the order of 0.75 (Table 2).

These SEC results confirm that LC PEAT gives a pure fraction of cyclic products for which separation is exclusively directed by architecture.

To have more information on the chemical composition of these products, the linear precursor, the crude cyclization product and the two fractions obtained by preparative liquid chromatography were then analyzed by MALDI−TOF mass spectrometry.

MALDI−TOF Mass Spectrometry Characterization. The MALDI spectrum of the linear precursor is presented in Figure 5. The spectrum shows a number of peaks with a peak-to-peak mass increment of 104 g·mol^{-1}, corresponding to the mass of the styrene unit. This series presents a single distribution. The calculated

Table 3. MALDI−TOF Experimental and Theoretical Molar Masses of Ag^+-Ionized Polystyrenes with Various Structures

values of the av peak for the experimentally obsd series	assumed possible structure	DP	calcd molecular mass of the average peak
8421	$(H-(styrene)_n-initiator^a-(styrene)_n-H,Ag)^+$	75	8422.2
8497	$(H-(styrene)_n-initiator-(styrene)_n-DDPE-H,Ag)^+$	74	8496.2
8497	$(styrene)_n-initiator-(styrene)_n-H-DDPE-H,Ag^+$	74	8496.2

[a] Initiator obtained by reaction of DDPE with 2 equiv of *sec*-BuLi.

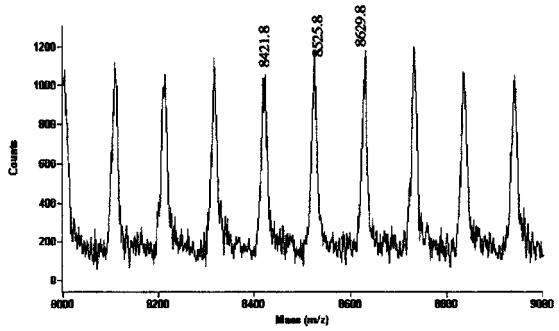


Figure 5. Expansion MALDI−TOF mass spectrum of the linear precursor.

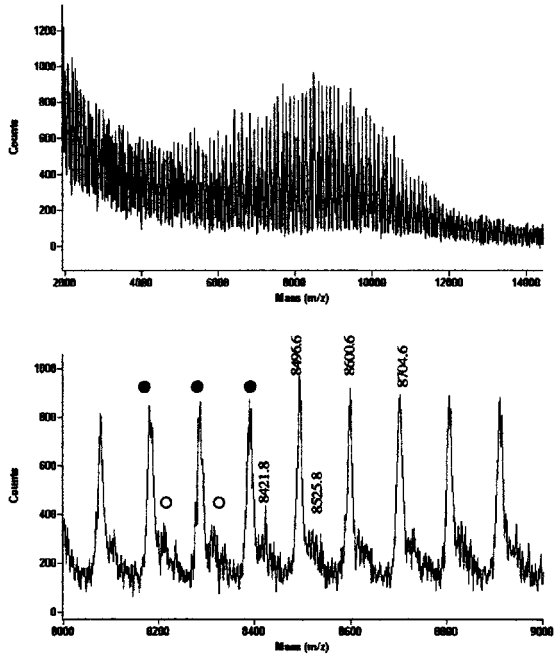


Figure 6. MALDI−TOF mass spectra of crude cyclization product: ○, series 1; ●, series 2.

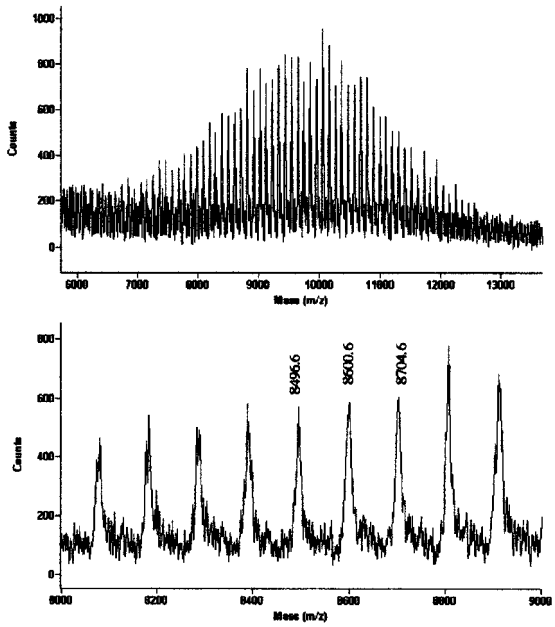


Figure 7. MALDI−TOF mass spectra for cyclic products obtained by preparative liquid chromatography.

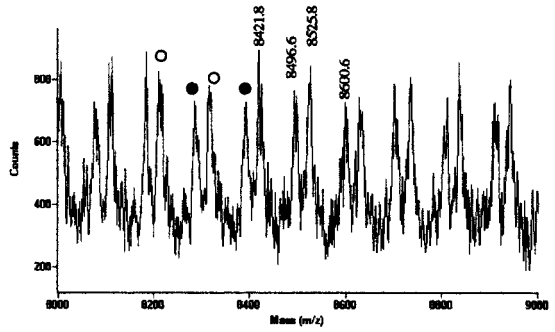


Figure 8. Expansion MALDI−TOF mass spectrum of linear products after preparative separation: ○, series 1; ●, series 2.

and experimental mass numbers are in good agreement (Table 3), and the mass spectrum corresponds to the proposed chemical structure $(H-(styrene)_n-initiator-(styrene)_n-H,Ag^+)$.

The MALDI spectrum of the crude products of cyclization is presented in Figure 6: two distributions are presented. A very small fraction of residual linears (series 1) is present in the cyclization products. The major distribution (series 2) could be assigned to the reaction with 1 mol of DDPE. This distribution might correspond to the two following isomeric forms: the cyclic product and the linear precursor with an unsaturated DDPE end group $(H-(styrene)_n-initiator-(styrene)_n-DDPE-H,Ag^+)$.

Then, the two fractions obtained by preparative liquid chromatography were subjected to MALDI−TOF mass spectrometry. The spectrum of the cyclic fraction is presented in Figure 7 and of the linear fraction in Figure 8.

The MALDI spectrum of the cyclic product fraction shows only one distribution (good agreement between the experimental and the theoretical molar masses). The very small fraction of residual linears, which is present in the crude cyclization products has disappeared. This result confirms the high purity of the sample obtained by preparative liquid chromatography.

The MALDI spectrum of the linear product fraction shows two series. The main series (series 1) corresponds to the "deactivated" linear precursor $(H-(styrene)_n-initiator-(styrene)_n-H,Ag^+)$. The other peak series (series 2) is believed to correspond to the linear precursor that reacted with DDPE (monoaddition) $(H-(styrene)_n-initiator-(styrene)_n$-DDPE$-H,Ag^+)$ but did not cyclized.

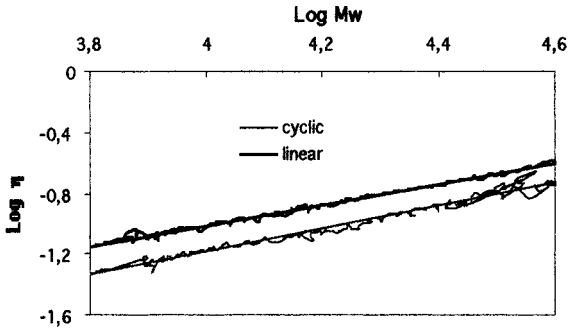


Figure 9. Intrinsic viscosities of linear and macrocyclic polystyrenes as a function of molar mass.

MALDI−TOF mass spectrometry results confirm that LC PEAT is a way to isolate cyclic products from the crude cyclization mixture.

Viscosity Measurements. Viscometric experiments were carried out by SEC (viscometry detector) in THF, a good solvent of polystyrene at 30 °C. The two fractions of linear and cyclic products obtained by preparative liquid chromatography were analyzed.

Figure 9 represents the Mark−Houwink plot (log $[\eta]$ vs log M) of cyclic and linear products. The graphic results in straight but not quite parallel lines. The Mark−Houwink parameter a is equal to 0.73 for the cyclic polystyrene and 0.68 for the linear products. These values are higher that those obtained in benzene[45] at 25 °C and close to those obtained in THF[48] at 25 °C; moreover, the theoretical value for cyclic products is not really known.

The ratios g' of the intrinsic viscosity of the cycles to that of the linear products with the same molar mass $g' = [\eta]_C/[\eta]_L$ are in the range 0.66−0.69, increasing slightly with the molar mass. The SEC and viscometric data confirm previous results.[12,48]

Theoretical calculations[46,47] for dilute solutions under Θ conditions have given a value of g' of about 0.66. Moreover, viscometric experiments performed by Lutz and colleagues[48] in THF have given a Mark−Houwink parameter and ratio g' values in agreement with this work. These results confirm the absence of contamination of the cyclic polymers by linear chains.

Conclusion

The coupling of two-ended living polystyryllithium with DDPE is presented in order to prepare macrocycles. The experiments were performed using simplified conditions in a drybox apparatus leading to macrocycles with a high yield. Using two different liquid chromatography techniques and MALDI−TOF mass spectrometry, macrocyclic polystyrenes were accurately analyzed. Separation of the macrocycles from the linear precursor and polycondensates was carried out using preparative liquid chromatography at the exclusion−adsorption transition point. SEC of the fraction of macrocycles showed the presence of products with twice and third the expected molar mass indicating the cyclic nature of the polycondensates. The chemical composition was obtained by MALDI−TOF mass spectrometry that confirmed, in addition with viscometric experiments, the isolation of highly pure cyclic polymers. For the first time, combination of these different analytical techniques gives proofs to previous results concerning the synthesis of macrocycles and provides information (not accessible with the classical techniques) on the exact composition of these products. Using this procedure, the synthesis of functionalized macrocycles can be achieved with a good control and synthesis of more complex architectures (multicyclic polymers, cyclic-based networks) is currently under investigation.

References and Notes

(1) Semlyen, J. A. *Cyclic Polymers*; Elsevier: New York, 1986.
(2) Semlyen, J. A. *Large Ring Molecules*; Wiley: New York, 1996.
(3) Ederle, Y.; Naraghi, K. S.; Lutz, P. J. *Synthesis of Polymers: Materials Science and Technology Series*; Wiley: 1999; p 622.
(4) Kramer, H. A. *J. Chem. Phys.* **1946**, *14*, 415.
(5) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(6) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.
(7) Semlyen, J. A. *Adv. Polym. Sci.* **1976**, *21*, 41.
(8) Sigwalt, P.; Masure, M.; Moreau, M.; Bischoff, R. *Makromol. Chem. Rapid Commun.* **1993**, *73*, 147.
(9) Hild, G.; Kohler, A.; Rempp, P. *Eur. Polym. J.* **1980**, *16*, 525.
(10) Geiser, D.; Höcker, H. *Macromolecules* **1980**, *13*, 653.
(11) Vollmert, B.; Huang, J. X. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 467.
(12) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.
(13) Quirk, R. P.; Ma, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 10.
(14) Bedha, M. C.; Gibson, H. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (1), 588.
(15) Hogen-Esch, T. E.; Sundarajan, J.; Toreki, W. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 23.
(16) Ohtani, H.; Kotsuji, H.; Momose, H.; Matsushita, Y.; Noda., I.; Tsuge, S. *Macromolecules* **1999**, *32*, 6541.
(17) Roovers, J.; Toporowski, P. M. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 1251.
(18) El Madani, A.; Favier, J.-C.; Hémery, P.; Sigwalt, P. *Polym. Int.* **1992**, *27*, 353.
(19) Quirk, R. P.; Ma, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 976.
(20) Gan, Y. D.; Zöller, J.; Yin, R.; Hogen-Esch, T. E. *Macromol. Symp.* **1994**, *77*, 93.
(21) Ma, J. In *The Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press Publ.: Boca Raton, FL, 1996; Vol. 4, p 3882.
(22) Iatrou, H.; Hadjichristidis, N. *Polym. Prepr. (Am Chem. Soc., Div. Polym. Chem.)* **1999**, *40* (2), 1059.
(23) Deffieux, A.; Schappacher, M.; Rique-Lurbet, L. *Polymer* **1994**, 35, 4562.
(24) Deffieux, A.; Beinat, S.; Schappacher, M. *Macromol. Symp.* **1997**, *118*, 247.
(25) Hadziioannou, G.; Cotts, P. M.; Brinke, G.; Han, C. C.; Lutz, P.; Strazielle, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 493.
(26) McKenna, G. B.; Plazek, D. J. *Polym. Commun.*
(27) Karas, M.; Hillenkamp, F. *Anal. Chem.* **1988**, *60*, 2299.
(28) Danis, P. O.; Karr, D. E.; Mayer, F.; Holle, A.; Watson, C. H. *Org. Mass Spectrom.* **1992**, *27*, 843.
(29) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Rapid Commun. Mass Spectrom.* **1994**, *8*, 1011.
(30) Dourges, M. A.; Charleux, B.; Vairon, J. P.; Blais, J. C.; Bolbach, G.; Tabet, J. C. *Macromolecules* **1999**, *32*, 2495.
(31) Pasch, H.; Deffieux, A.; Ghahary, R.; Schappacher, M.; Rique-Lurbet, L. *Macromolecules* **1997**, *30*, 98.
(32) Berek, D. *Macromol. Symp.* **1996**, *110*, 33.
(33) Pasch, H. *Macromol. Symp.* **1996**, *110*, 107.
(34) Pasch, H.; Brinkmann, C.; Gallot, Y. *Polymer* **1993**, *34*, 4100.
(35) Pasch, H.; Deffieux, A.; Henze, I.; Schappacher, M.; Rique-Lurbet, L. *Macromolecules* **1996**, *29*, 8776.
(36) Krüger, R.-P.; Much, H.;. Schulz, G. *J. Liq. Chromatogr.* **1994**, *17*, 3069.
(37) Ma, J. *Macromol. Symp.* **1995**, *91*, 41.
(38) Schulz, G. G. H.; Höcker, H. *Makromol. Chem.* **1977**, *178*, 2589.
(39) de Gennes, C. *C. R. Acad. Sci. Paris* **1990**, *310*, 1327.
(40) ten Brinke, G.; Hadziioannou, G. *Macromolecules* **1987**, *20*, 480.
(41) Obriot, I.; Favier, J. C.; Sigwalt, P. *Polymer* **1987**, *28*, 2093.
(42) Quirk, R. P.; Yoo, T.; Lee, B. *J. Macromol. Sci. Pure Appl. Chem.* **1994**, A31, 911.
(43) Baran, K.; Laugier, S.; Cramail, H. *Macromol. Chem. Phys.* **1999**, 200, 2074.

(44) Skvortsov, A. M.; Gorbunov, A. A. *J. Chromatogr.* **1990**, *507*, 487.
(45) Einaga, Y.; Koyama, H.; Konishi, T.; Yamakawa, H. *Macromolecules* **1989**, *22*, 3419.
(46) Casassa, E. F. *J. Polym. Sci., Part A* **1965**, *3*, 315.
(47) Bloomfield, V.; Zimm, B. H. *J. Chem. Phys.* **1966**, *44*, 315.
(48) Lutz, P.; McKenna, G. B.; Rempp, P.; Strazielle, C. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 599.

MA000059Q