Syntheses of Tadpole- and Eight-Shaped Polystyrenes Using Cyclic Polystyrene as a Building Block

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ABSTRACT: The intramolecular cyclization of α-carboxyl, *ω*-amino heterodifunctional polystyrene was carried out to obtain cyclic polystyrene having an amide moiety in the main chain. The amide moiety was reduced with lithium aluminum hydride to give macrocyclic amine. The reactions of the macrocyclic amine with carboxylic-terminated polystyrene and glutaric acid gave tadpole- and eight-shaped polystyrenes, respectively. These macromolecular architectures were characterized by NMR, IR, and GPC analysis.

Introduction

It is known that chain topology plays an important role in determining polymer properties. Polyethylene prepared by organometallic catalysts is a structurally regular chain with very few branch points. It is a highly crystalline material with a correspondingly high density. On the other hand, a high-pressure, radical-initiated polymerization of ethylene gives a highly branched polyethylene that has a much lower crystalline content and density. A number of studies have been reported on the preparation of polymers with complex chain architectures, including dendrimers,[1,2] hyperbranched polymers,[3] star polymers,[4−6] and cyclic polymers.[7−14]

Recently, we reported briefly the synthesis of an α-carboxyl, *ω*-amino heterodifunctional polystyrene derived from an α-diethyl acetal, *ω*-amino heterodifunctional polystyrene and its intramolecular cyclization to obtain cyclic polystyrene (Scheme 1).[15] The cyclic product can be purified easily by silica gel column chromatography since unreacted material or chain-extended byproducts possess a terminal amine functionality that interacts with SiO_2.

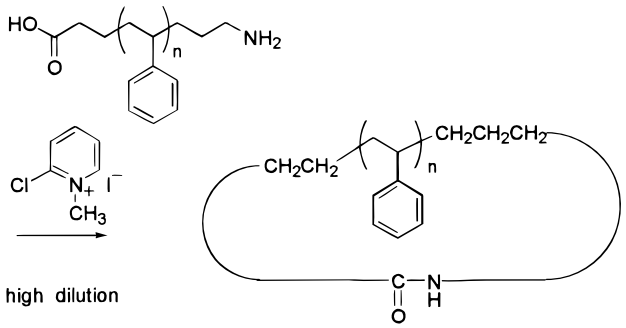
Our idea is to use this cyclic polystyrene having an amide moiety in the chain as a building block for further macromolecular architectures because the amide moiety is a useful functional group for chemical modification. In this paper, we report the reduction of the amide moiety of the cyclic polystyrene to obtain the macrocyclic amine and its derivatizations to tadpole- and eight-shaped polystyrenes.

Experimental Section

Instrumentation. Infrared spectra were recorded on JASCO IR-700 infrared spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL EX-270 nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) was carried out with a set of Tosoh TSK-gel G2500H and G2000H columns using tetrahydrofuran (THF) and standard polystyrenes as an eluent and references, respectively.

α-Diethyl Acetal, *ω*-Amino Heterodifunctional Polystyrene (1). In a typical example, into a solution of styrene (4.5 g, 45 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.35 g, 3.0 mmol) in 50 mL of freshly distilled benzene was introduced 3-lithiopropionaldehyde diethyl acetal (2.2 mmol in 10 mL of ether) prepared according to the literature[13] to initiate the polymerization. A rapid red coloration of the solution was observed. The reaction mixture was stirred under nitrogen at room temperature for 2 h and then cooled to −20 °C. 2,2,5,5-Tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane[16] (1.2 g, 4.4 mmol) was added to the mixture using an airtight syringe. The color of the reaction mixture changed from deep red to pale yellow. The mixture was washed successively with aqueous hydrochloric acid, water, 5% aqueous sodium bicarbonate, and water. The organic layer was dried with anhydrous magnesium sulfate and placed under reduced pressure to remove the solvents to give a pale yellow viscous material, which was dissolved in a mixture of ethanol and THF (4:1 by volume). The resulting solution was stirred at room temperature for 12 h to complete the cleavage of the N−Si bonds and placed under reduced pressure to remove the solvents. The residue was charged on a silica gel column using dichloromethane as an eluent. After the first band was collected to remove the polystyrene that was not aminated, the eluent was changed to a mixture of chloroform and ethanol (9:1 by volume) and the second band was collected to give **1** (4.5 g, 92%) as a white powder: ^{1}H NMR ($CDCl_3$, *δ*) 1.1 (m, CH_3), 1.2−2.5 (m, CH and CH_2), 3.0 (brs, NCH_2), 3.3−3.5 (m, OCH_2), 4.3 (m, CH), 6.3−7.3 (phenyls).

Scheme 1



α-Diethyl Acetal, *ω*-Benzyloxycarbonylamino Heterodifunctional Polystyrene (2). In a typical example, a mixture of **1** (M_n = 2240) (4.5 g, 2.0 mmol), 80 mL of toluene, 60 mL of 1% aqueous sodium hydroxide, and benzyloxycarbonyl chloride (0.36 g, 2.2 mmol) was stirred vigorously at room temperature for 7 h. The organic layer was washed with diluted aqueous hydrochloric acid, dried with anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using dichloromethane as an eluent. The first band

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was collected to give **2** (4.6 g, 98%) as a white powder: ^{1}H NMR ($CDCl_3$, δ) 1.1 (m, CH_3), 1.2−2.4 (m, CH and CH_2), 3.0 (brs, NCH_2), 3.3−3.5 (m, OCH_2), 4.3 (m, CH), 4.6 (m, NH), 5.0 (s, $COOCH_2$), 6.3−7.2 (m, phenyls), 7.3 (s, phenyls).

α-Formyl, ω-Benzyloxycarbonylamino Heterodifunctional Polystyrene (3). In a typical example, a mixture of **2** (M_n = 2360) (3.8 g, 1.6 mmol), 100 mL of THF, and 1 mL of 1% aqueous hydrochloric acid was heated under reflux for 16 h. It was poured into 200 mL of water and extracted with benzene. The organic layer was dried with anhydrous magnesium sulfate and placed under reduced pressure to remove the solvent to give **3** (3.5 g, 94%) as a white solid: ^{1}H NMR ($CDCl_3$, δ) 1.2−2.4 (m, CH and CH_2), 2.9 (brs, NCH_2), 4.4 (brs, NH), 5.0 (s, $COOCH_2$), 6.3−7.2 (m, phenyls), 7.3 (s, phenyls), 9.5 (brs, CHO).

α-Carboxyl, ω-Benzyloxycarbonylamino Heterodifunctional Polystyrene (4). In a typical example, a solution of **3** (M_n = 2290) (3.0 g, 1.3 mmol) and *m*-chloroperbenzoic acid (mCPBA) (0.26 g, 1.5 mmol) in 50 mL of dichloromethane was stirred at room temperature for 18 h and then washed successively with saturated aqueous sodium thiosulfate, saturated aqueous sodium bicarbonate, brine, and water. The organic layer was dried over anhydrous magnesium sulfate and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using ethyl acetate as an eluent. The first band was collected to give **4** (2.8 g, 93%) as a white powder: ^{1}H NMR ($CDCl_3$, δ) 1.2−2.3 (m, CH and CH_2), 3.0 (brs, NCH_2), 4.4 (brs, NH), 5.0 (s, $COOCH_2$), 6.3−7.2 (m, phenyls), 7.3 (s, phenyls).

α-Carboxyl, ω-Amino Heterodifunctional Polystyrene (5). In a typical example, a mixture of **4** (M_n = 2300) (1.0 g, 0.44 mmol), 30 mL of acetic acid containing 30 wt % of hydrogen bromide, and 20 mL of dichloromethane was stirred at room temperature for 12 h. It was poured into water and extracted with dichloromethane. The organic layer was washed with 1% sodium hydroxide solution, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using ethyl acetate as an eluent. After the first band was collected to remove the benzyl bromide, the eluent was changed to a mixture of chloroform and ethanol (9:1 by volume) and the second band was collected to give **5** (0.60 g, 63%) as a white powder: ^{1}H NMR ($CDCl_3$, δ) 1.2−2.4 (m, CH and CH_2), 5.1 (brs, NH_2), 6.3−7.2 (phenyls).

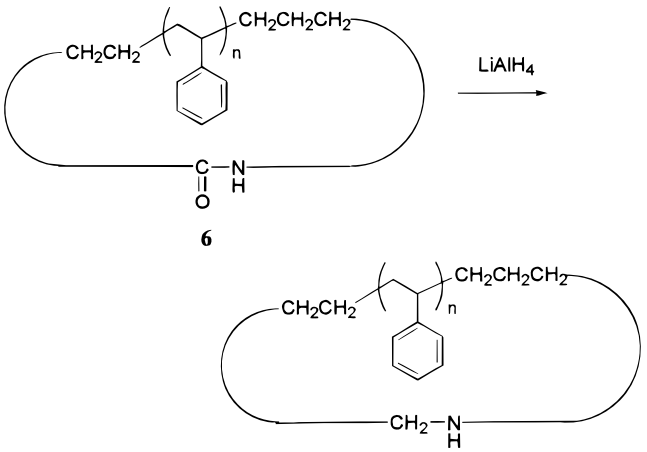
Cyclic Polystyrene (6). In a typical example, into a solution of triethylamine (32 mg, 0.32 mmol) and 1-methyl-2-chloropyridinium iodide (42 mg, 0.16 mmol) in 1000 mL of dichloromethane was added **5** (M_n = 2170) (0.30 g, 0.14 mmol) dissolved in 1000 mL of dichloromethane over a period of 10 h under reflux with vigorous stirring. After the mixture was concentrated to ca. 200 mL, it was washed with dilute aqueous hydrochloric acid, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using chloroform as an eluent. The first band was collected to give **6** (0.18 g, 62%) as a colorless solid: ^{1}H NMR ($CDCl_3$, δ) 1.2−2.3 (m, CH and CH_2), 3.0 (brs, NCH_2), 4.9 (brs, NH), 6.3−7.2 (phenyls).

Macrocyclic Amine (7). In a typical example, into a suspension of lithium aluminum hydride (40 mg, 1.0 mmol) in 10 mL of ether was added **6** (M_n = 2150) (0.17 g, 0.8 mmol) and the mixture was heated under reflux for 5 h. The reaction mixture was cooled to 0 °C, and saturated magnesium sulfate solution was added dropwise to the solution. The mixture was extracted with dichloromethane; then the organic layer was dried with magnesium sulfate and placed under reduced pressure to remove the solvent to give **7** (0.15 g, 89%) as a white powder: ^{1}H NMR ($CDCl_3$, δ) 1.1−2.3 (m, CH and CH_2), 4.6 (brs, NH), 6.3−7.2 (phenyls).

Tadpole-Shaped Polystyrene (8). In a typical example, a mixture of carboxyl-terminated polystyrene **4** (M_n = 2300) (0.12 g, 0.05 mmol), **7** (M_n = 2140) (0.11 g, 0.05 mmol), 1-methyl-2-chloropyridinium iodide (21 mg, 0.08 mmol), and triethylamine (12 mg, 0.12 mmol) in 15 mL of dichloromethane was heated under reflux for 24 h. The reaction mixture was washed with water and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using dichloromethane as an eluent. After the first band was collected, the eluent was changed to ethyl acetate and the second band was collected. It was then charged on an alumina column using dichloromethane as an eluent. The first band was collected to give tadpole-shaped polystyrene **8** as a white powder (0.10 g, 43%): ^{1}H NMR ($CDCl_3$, δ) 1.2−2.3 (m, CH and CH_2), 3.0 (brs, NCH_2), 4.5 (brs, NH), 5.1 (s, $COOCH_2$), 6.3−7.2 (phenyls), 7.3 (s, phenyls).

Eight-Shaped Polystyrene (9). In a typical example, a mixture of cyclic polystyrene **7** (M_n = 2140) (86 mg, 0.04 mmol), glutaric acid (3.2 mg, 0.02 mmol), 1-methyl-2-chloropyridinium iodide (60 mg, 0.06 mmol), and triethylamine (10 mg, 0.10 mmol) in 15 mL of dichloromethane was heated under reflux for 24 h. The reaction mixture was washed with water and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using ethyl acetate as an eluent, and the first band was collected. This was charged on an alumina column using dichloromethane as an eluent. The first band was collected to give eight-shaped polystyrene **9** as a white powder (43 mg, 49%): ^{1}H NMR ($CDCl_3$, δ) 0.7−2.3 (m, CH and CH_2), 2.8−3.0 (m, NCH_2), 6.3−7.3 (phenyls).

Scheme 2. Synthesis of Macrocyclic Amine 7



Results and Discussion

Macrocyclic Amine (7). Cyclic polystyrene **6** was prepared by a five-step method with an overall yield of 30−35% from α-diethyl acetal, ω-amino heterodifunctional polystyrene, which was obtained by the living anionic polymerization of styrene using 3-lithiopropionaldehyde diethyl acetal and 2,2,5,5-tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane, as an initiator and a terminator, respectively.[15] We reduced the amide linkage of **6** with lithium aluminum hydride to obtain macrocyclic amine **7**. This gave a material with the nucleophilicity of an amine for further reaction (Scheme 2). The ^{1}H NMR spectrum of the obtained macrocyclic amine **7** is shown in Figure 1 together with that of **6**. The peaks at 3.0 and 4.9 ppm can be assigned to methylene protons adjacent to nitrogen and amide protons, respectively (Figure 1a). After reduction, these peaks disappeared completely and a new peak at 4.5 ppm assignable to amino protons emerged (Figure 1b). The IR spectrum of the reduced product did not exhibit an amide carbonyl peak at 1643 cm^{-1}, which was present in macrocyclic amide **6**. The peak at 172.5 ppm in the ^{13}C NMR spectrum due to the amide carbonyl carbon disappeared completely. These observations confirm the transformation of **6** to macrocyclic amine **7**.

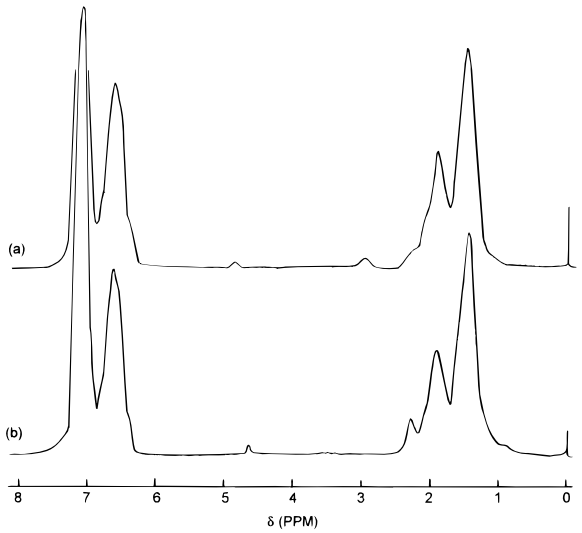
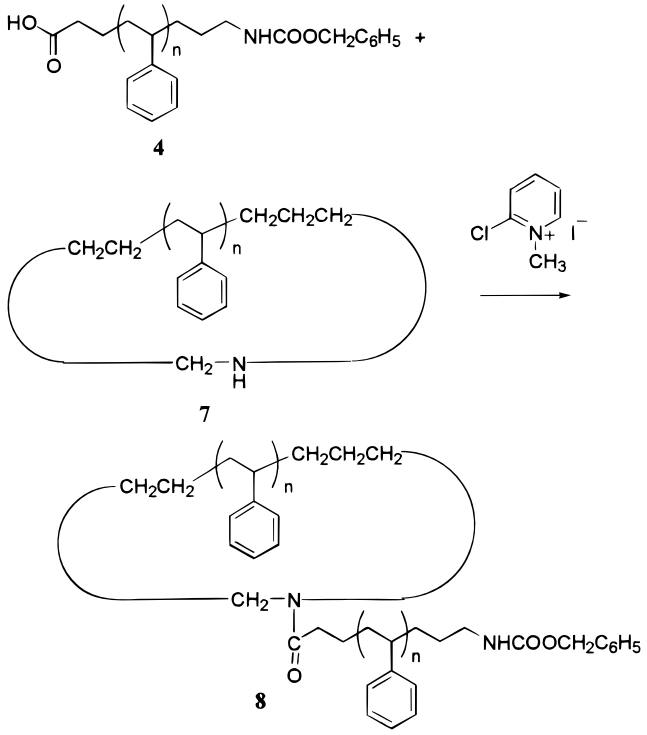


Figure 1. 270-MHz ^{1}H NMR spectra of (a) cyclic polystyrene **6** of M_n = 2250 and (b) macrocyclic amine **7** of M_n = 2250. Solvent: $CDCl_3$.

Scheme 3. Synthesis of Tadpole-Shaped Polystyrene 8



Tadpole-Shaped Polystyrene. The coupling reaction of **7** with carboxyl-terminated linear polymer gave a tadpole-shaped polymer. We used polystyrene **4** (parent polymer of **7**) as a carboxyl-terminated linear polymer with the same degree of polymerization as **7**. The coupling reaction was carried out using 2-chloro-1-methylpyridinium iodide in dichloromethane under reflux (Scheme 3). The product was purified by chromatography using both silica gel and alumina columns. The obtained tadpole polystyrene **8** was characterized by ^{1}H NMR, IR, and GPC analysis. The molecular weight distribution of **8** remained narrow (M_w/M_n = 1.22), suggesting that the product did not contain macrocyclic amine **7** or linear carboxyl-terminated polystyrene **4**, as shown in Figure 2. Figure 3 shows the ^{1}H NMR spectrum of **8** along with peak assignments. The IR spectrum showed absorption bands at

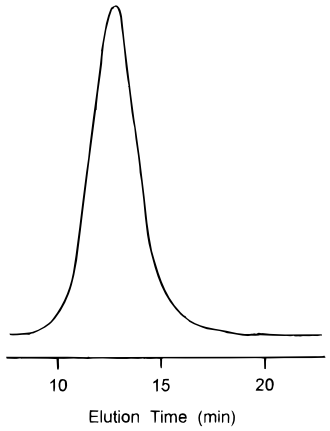


Figure 2. GPC curve of tadpole-shaped polystyreyrene **8** of M_n = 4420. Solvent: THF.

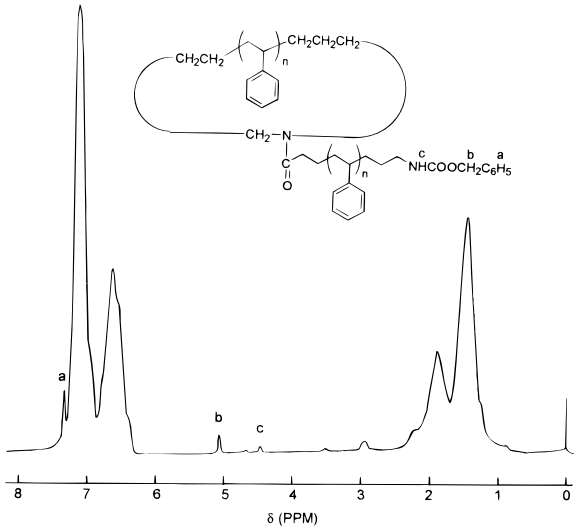


Figure 3. 270-MHz ^{1}H NMR spectrum of tadpole-shaped polystyrene **8** of M_n = 4420. Solvent: $CDCl_3$.

1700 and 1610 cm^{-1} due to carbonyl groups of benzyl carbamates and amides, respectively.

Eight-Shaped Polystyrene. Eight-shaped polymers have been prepared by the bimolecular coupling reactions of a two-ended living dicarbanionic polystyrene[17] or polyisoprene[18] with tetrachlorosilane as a tetrafunctional reagent. Another strategy for obtaining an eight-shaped polymer is the stepwise double cyclization technique reported by Hémery et al.[19] Recently, Schappacher and Deffieux reported the controlled synthesis of bicyclic eight-shaped poly(chloroethyl vinyl ether)s. Their strategy involved the preparation of a linear tetrafunctional precursor bearing two series of functional groups, which allowed formation of two rings per chain.[20]

Since our cyclic polystyrene has an amine functionality in the ring, eight-shaped polymers can be obtained by the one-step reaction between macrocyclic amine **7** and dicarboxylic acids such as glutaric acid (Scheme 4). The eight-shaped polystyrene **9** was purified by chromatography using silica gel and alumina columns and characterized by ^{1}H NMR, ^{13}C NMR, IR, and GPC analysis. Figure 4 shows the ^{1}H NMR spectrum of eight-shaped polystyrene **9**. The peak around 2.8 ppm is assigned to the methylene protons adjacent to nitrogen. The IR spectrum exhibited the amide carbonyl absorption at 1610 cm^{-1}. The absence of carboxyl

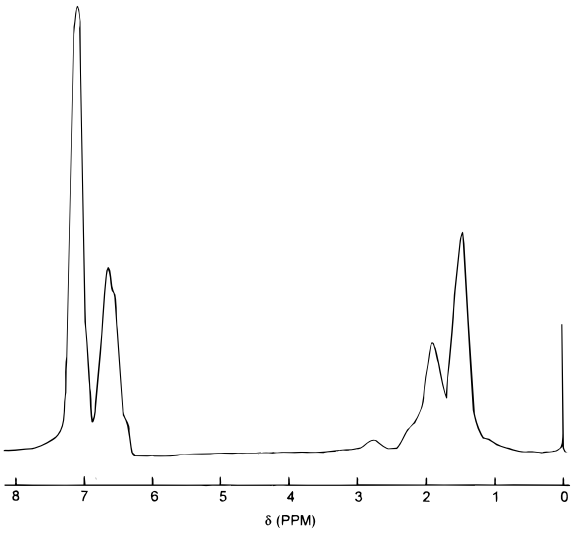
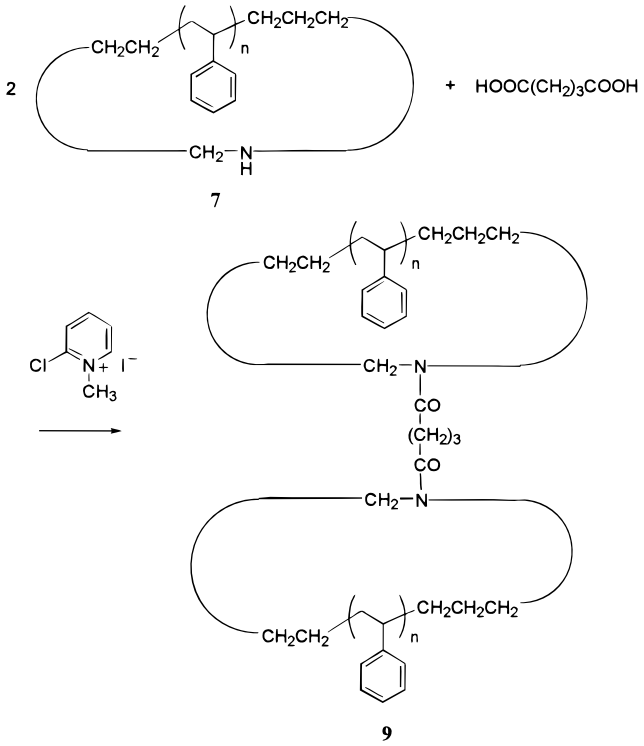


Figure 4. 270-MHz ^{1}H NMR spectrum of eight-shaped polystyrene **9** of $M_n = 4370$. Solvent: $CDCl_3$.

Scheme 4. Synthesis of Eight-Shaped Polystyrene 9



groups was confirmed by the ^{13}C NMR spectrum, which exhibited only an amide carbonyl peak at 172 ppm.

Hydrodynamic Volume. Cyclic polymers exhibit a slower elution time than linear ones in gel permeation chromatography (GPC). This is generally attributed to the smaller hydrodynamic volumes of cyclic chains as compared with the linear chains.[10] Comparison of the apparent molecular weights obtained from GPC using polystyrene standards with the true one gives useful information about the hydrodynamic volume, which is related to the elution volume. It has been pointed out that some polystyrenes with terminal functionalities such as amino groups are difficult to analyze by GPC because of physical absorption effects.[21] In fact, the GPC chromatogram of our amino-terminated polystyrene **1** exhibited a tailing. We chose polystyrenes **2**, **6**, **8**, and **9** as representatives of linear, ring, tadpole-shaped, and eight-shaped polystyrenes, respectively. The GPC chromatograms of these polymers were narrow and symmetrical. The number-average molecular weight of **1** was determined from the peak area ratio of headgroup diethyl acetal protons to aromatic protons in its ^{1}H NMR spectrum.[15] The molecular weights of **2**, **6**, **8**, and **9** were calculated using the value of their parent polymer **1**, assuming that the degree of polymerization remained unchanged during the polymer reactions. Table 1 summarizes the calculated (true) molecular weights ($M_{n,NMR}$) based on the degree of polymerization of **1**, the apparent molecular weights ($M_{n,GPC}$) obtained from GPC with polystyrene standards, and the value of $M_{n,GPC}/M_{n,NMR}$.

Table 1. Molecular Weights of the Linear Parent Polymer and Its Derivatives Determined by NMR and GPC

polymer	architecture	$M_{n,NMR}$	$M_{n,GPC}$	$M_{w,GPC}/M_{n,GPC}$	$M_{n,GPC}/M_{n,NMR}$
Degree of Polymerization of Parent Polymer **1** = 20					
2	linear	2360	2250	1.09	0.95
6	ring	2250	1790	1.12	0.83
8	tadpole-shaped	4420	3800	1.22	0.86
9	eight-shaped	4370	3060	1.26	0.70
Degree of Polymerization of Parent Polymer **1** = 27					
2	linear	3110	3170	1.10	1.02
6	ring	2900	2350	1.14	0.81
8	tadpole-shaped	5920	5030	1.23	0.85
9	eight-shaped	5870	4050	1.24	0.69
Degree of Polymerization of Parent Polymer **1** = 33					
2	linear	3710	3600	1.07	0.97
6	ring	3500	2910	1.18	0.83
8	tadpole-shaped	7130	6130	1.20	0.86
9	eight-shaped	7070	4810	1.23	0.68

The value of $M_{n,GPC}/M_{n,NMR}$ is considered to be a measure of relative hydrodynamic volume. No dependence was found between $M_{n,GPC}/M_{n,NMR}$ values and degree of polymerization for **2**, **6**, **8**, or **9**. It is clear that the value $M_{n,GPC}/M_{n,NMR}$ decreased in the sequence of linear, tadpole-shaped, ring, and eight-shaped polymer, indicating that the hydrodynamic volume decreases in this sequence. Schappacher and Deffieux prepared bicyclic eight-shaped poly(chloroethyl vinyl ether)s and reported that the hydrodynamic volume of the eight-shaped polymer is not noticeably lower than that of a monocyclic polymer of the same molecular weight.[20] At the present, we have no explanation for the different results obtained here. The nature of the chain may be the reason, since the macromolecular architectures here are based on polystyrene, which has a relatively rigid chain compared to poly(chloroethyl vinyl ether). Deffieux et al. reported that the experimental $\langle G \rangle$ value, M_p(cycle)/M_p(linear), for polystyrene was lower than that for poly(chloroethyl vinyl ether).[12]

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