# Synthesis and Characterization of Narrow Molecular Weight Distribution Polystyrene–Poly(dimethylsiloxane) Macrocyclic Block Copolymers and Their Isobaric Precursors

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ABSTRACT: The first synthesis of a well-defined and monodisperse macrocyclic polystyrene (PS)–poly(dimethylsiloxane) (PDMS) block copolymer is reported. The two-ended linear PDMS-*b*-PS-*b*-PDMS precursor is prepared through initiation of styrene by lithium naphthalenide in THF at −78 °C, followed by addition of hexamethylcyclotrisiloxane ($D_3$) to the LiPSLi. The cyclization is carried out by reaction with dichlorodimethylsilane at high dilution. For higher MW linear precursors, side reactions were observed but could be prevented by capping the highly reactive LiPSLi with 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (EDS) followed by addition of $D_3$. The macrocyclic PS–PEDS–PDMS–PEDS tetrablock copolymer is synthesized in a similar manner. Both macrocyclic block copolymers and their linear precursors are characterized by SEC and NMR. In addition to smaller (17–31%) hydrodynamic volumes observed by SEC, distinct differences between a macrocyclic and its linear block copolymer are shown by proton, $^{13}C$, and $^{29}Si$ NMR.

## Introduction

Narrow molecular weight distribution macrocyclic block copolymers containing two incompatible blocks are of interest for several reasons. First, macrocyclic block copolymers could help to provide insight into the arrangement of block copolymers in microdomains.[1] Linear triblocks can be arranged in microdomains as bridging chains and looping chains (Figure 1). However, diblock rings can only form looping chains. Second, macrocyclic block copolymers are of interest in that the radius of gyration of one of the blocks in solution could be determined by eliminating light scattering of the second block by an isorefractive solvent. Thus, theoretical predictions on the expansion of rings may be tested.[2-8]

Based on these considerations, narrow molecular weight and block distribution macrocyclic polystyrene (PS)–poly(dimethylsiloxane) (PDMS) and its isobaric linear PDMS–PS–PDMS triblock copolymers were chosen as the target polymers. Such block copolymers exhibit a large difference in compatibility between PDMS ($\delta = 7.3$) and PS ($\delta = 9.1$), compared to PS and *cis*-1,4-PBD ($\delta_{PBD} = 8.6$); thus a stronger phase separation is expected.[9] In addition, due to a large difference in refractive index between PS and PDMS, the scattering of one of the blocks may be suppressed by proper selection of the appropriate isorefractive solvents.

A synthesis of macrocyclic PS–PDMS block copolymers has been reported.[10] In this case the macrocyclic copolymers were synthesized by ring–chain equilibration in basic media of PDMS–PS–PDMS block copolymers containing potassium silanolate end groups. However, such a procedure in addition to producing some cyclic block copolymers also produced segmented linear block copolymers of increased molecular weight. Furthermore, these block copolymers contained rather small polystyrene and PDMS blocks. Also, the overall distributions were wide, consistent with the synthesis methods.

In order to make physiochemical (i.e., light scattering) and morphological (TEM) studies more meaningful, we have attempted to synthesize a series of narrow distribution macrocyclic PS–PDMS and isobaric PDMS–PS–PDMS block copolymers suitable for such studies.

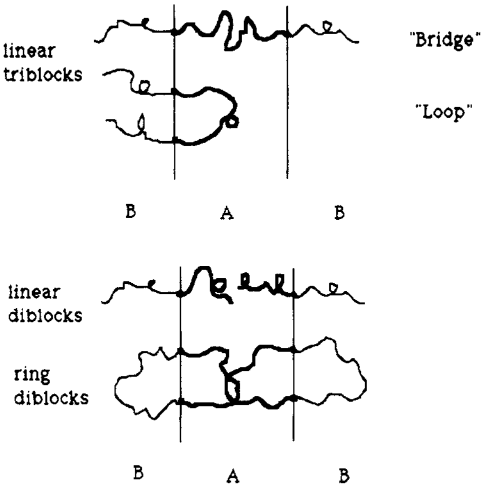

**Figure 1.** Bridging and looping chains in linear and macrocyclic block copolymers.

## Experimental Section

The purification of solvents, monomers, and other reagents was carried out as reported previously.[11]

Hexamethylcyclotrisiloxane ($D_3$; Aldrich), 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (EDS; Petrarch), and ethylene oxide (Aldrich) were purified by distilling from $CaH_2$ into ampules before use.

*n*-Butyllithium (Aldrich) was clarified by filtering the solution through a coarse frit and was then divided into ampules. Pure *tert*-butyllithium was obtained by sublimation and dissolution into pure hexane to give a solution that was divided into ampules.

Dichlorodimethylsilane (DCDMS) and chlorotrimethylsilane were stirred and distilled from $CaH_2$ and stored over $Na_2CO_3$ in a round-bottomed flask equipped with a Teflon stopcock and a ground-glass joint. Since DCDMS tends to react with glass surfaces, the purity of DCDMS cannot be checked by capillary column GC. Thus, 1 equiv of a living PS–PDMS block copolymer was reacted with $^1/_2$ equiv of the purified DCDMS. More than 99% of PS–PDMS–PS (ABA) block copolymer was formed without a low MW shoulder as measured by SEC, indicating that the coupling reagent was highly pure.

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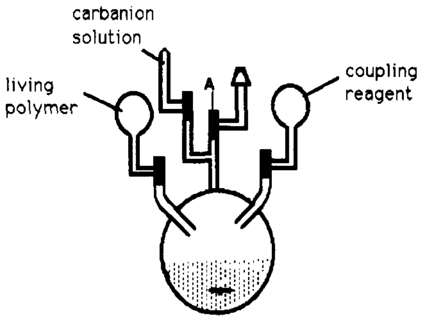


**Figure 2.** Apparatus used for the synthesis of macrocyclic PS-PDMS block copolymers.

**Initiators.** 1,4-Dilithio-1,1,4,4-tetraphenylbutane ($DD^{2-}$), $\alpha$-methylstyrene oligomeric dianion ($\alpha$-$MST^{2-}$), and lithium naphthalenide ($Li^+N^{\bullet-}$) were prepared as reported previously[12] and stored at -28 °C for $DD^{2-}$ and $\alpha$-$MST^{2-}$ and at -78 °C for $Li^+N^{\bullet-}$.

(Triphenylmethyl)lithium was prepared in a similar manner by reaction of $Ph_3CH$ with $n$-BuLi in THF.

**Synthesis of PS-PDMS AB and BAB Block Copolymers.** PS-PDMS AB and BAB block copolymers were prepared in vacuo by sequential anionic polymerizations of styrene and $D_3$. The AB and BAB polymers were synthesized using $t$-BuLi and lithium naphthalenide as initiators, respectively.

In order to reduce silanolate aggregation and synthesize larger quantities of macrocyclic copolymers, a large reaction flask (1000 mL) was used in this synthesis. A total of about 4-5 g of monomers (styrene and $D_3$) was used in each run. The flask was evacuated, and an initiator solution was added through a break-seal into the flask. The flask was then cooled to -78 °C, and fresh THF was distilled in from a solvent reservoir until about 400 mL of solution was collected. A known volume of purified styrene was slowly distilled onto the rapidly stirred initiator solution. A sample of PS taken by pouring about 25 mL of the living polymer solution into a side bulb was terminated with methanol immediately while still cold. The main flask was cooled to -40 °C, and a THF solution of $D_3$ or EDS was slowly added into the living PS solution. The orange-red color usually disappeared within several minutes as the solution was slowly warmed to room temperature. However, the orange-red color remained for a longer time when the carbanion concentration was high. The polymerization of $D_3$ proceeded at room temperature for 12 h so that almost all of the $D_3$ was polymerized. The concentration of living ends was generally between $10^{-3}$ and $10^{-4}$ M. Most of the colorless living polymer solution (about 300 mL) was poured into a larger side bulb that was closed off by a Teflon stopcock. This portion of the living polymer was coupled later to produce the AB macrocyclic block copolymer. The remaining portion (about 100 mL) was terminated by trimethylchlorosilane distilled through the vacuum line, giving the BAB linear block copolymer that serves as an isobaric reference for the macrocyclic block copolymer. The terminated block copolymer was precipitated in a large amount of methanol, then filtered, and dried in a vacuum oven for 24 h at 60 °C.

**Synthesis of PS-*b*-PDMS Macrocycles.** The BAB (PDMS-PS-PDMS) living silanolate block copolymer solution was reconnected to a cyclization apparatus (Figure 2), along with the coupling reagent ampule and a (triphenylmethyl)lithium washing solution ampule. After evacuation and flaming, the reaction bulb was cooled with a dry ice-isopropyl alcohol bath and about 300-400 mL of THF was distilled in. The stopcock was closed, and the apparatus was removed from the line. The solution was allowed to warm up to room temperature. A few drops of a red carbanion ($Ph_3CLi$) washing solution was added in, and the solution was shaken and allowed to contact the entire apparatus. This procedure was repeated until a light-pink color persisted. This indicated that the THF was absolutely proton and $O_2$ free. Protonic impurities could react with Si-Cl bonds, leading to imperfect coupling. The triphenylmethane generated is removed during polymer precipitation.

The main flask was cooled to 5-10 °C by an ice water bath so that the solutions from the ampules could be added without difficulties. The stopcocks controlling the addition of both difunctional living polymer and coupling reagent were opened, allowing the two solutions to add slowly such that the rates of addition of living polymer and DCDMS in moles per unit time were identical. The entire cyclization took about 2-3 h. Since there is no color indicator during cyclization, the coupling reagent and living polymer solutions were made in the same concentration and volume. On the other hand, since living silanolates are quite stable at room temperature, no special cooling precautions were required during this procedure. After cyclization, the crude polymer solution was concentrated in a rotary evaporator, precipitated in a large excess of methanol, filtered, and dried in a vacuum oven.

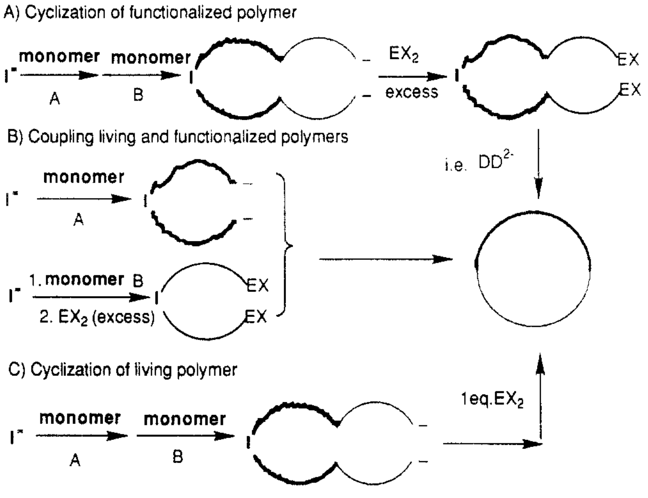
**Synthesis of a Macrocyclic PS-PEDS-PDMS Tetrablock Copolymer.** Following a polymerization of styrene initiated with lithium naphthalenide, a small sample (about 25 mL) taken from the solution was separated for analysis. An EDS-THF solution was then added into the remaining rapidly stirred difunctional living PS at -78 °C. The solution temperature was allowed to warm to -20 °C. The color of the solution changed from red to light pink within a few minutes. Upon warming to room temperature the solution became colorless immediately, indicating complete conversion into silanolate. The solution was allowed to stir at room temperature until no MW increase was observed by SEC (about 2 h). A $D_3$-THF solution was then introduced into the solution. After 8-12 h, the solution was divided into two portions. One was terminated by TMSCl. The other one was removed from the polymerization apparatus and reattached to the cyclization apparatus. The cyclization was done in a manner similar to that for the diblock ring. The polymer was characterized and fractionated as described above.

**Fractionation of Macrocyclic Block Copolymers.** The crude cyclization product was concentrated on a rotary evaporator and precipitated in a large excess of methanol. Thus, the low-MW impurities such as naphthalene, triphenylmethane, and unreacted $D_3$ monomer were separated from the polymer. The crude product (about 2-3 g) was dissolved in about 50 mL of THF. The solution was stirred rapidly, and methanol was slowly added in. The solution first became cloudy and then started to form a two-phase system. The upper phase contains mainly the more soluble cyclic polymer, while the lower phase is enriched in the high-MW "polycondensate". The solution was allowed to stand until the lower phase had completely settled out. The upper clear solution was then analyzed by SEC. If the high-MW shoulder was still present in the upper portion, more methanol was added until the high-MW shoulder was removed. Care was taken to ensure that the SEC peak maximum coincided exactly with that of the macrocycle in the crude product. The upper layer was carefully isolated by pipet, precipitated in a large excess of methanol, and dried in a vacuum oven. Approximately 0.5-1 g of cyclic polymer was obtained in each run.

**Characterization. Size-Exclusion Chromatography (SEC).** Size-exclusion chromatography (SEC) was performed on a Waters high-pressure liquid chromatography system consisting of a Waters 510 HPLC pump, a UK6 injector, a Waters 2-$\mu$m precolumn filter, Waters 500- and $10^4$-Å ultrastyragel columns, a Waters column heater module, a Waters 680 automated gradient controller, a Waters 410 refractive index detector, liquid flowmeter, and a Zenith PC interface for data collection. The linear range of separation of the two ultrastyragel columns (10 $\mu$m) was from $M_n$ = 500 to 50 000 for the 500-Å column and from $M_n$ = 40 000 to 500 000 for the $10^4$-Å column. The temperature of the columns was kept at 35 °C by a column heater. THF was used as the eluting solvent. The sample concentrations injected ranged from 0.2 wt % for samples of molecular weight above 25 000 to 0.5 wt % for samples of molecular weight under 25 000. All of the samples were filtered three times through a 0.5-$\mu$m filter before injection. In each run, about 10-25 $\mu$L was injected into the columns. Because differences in flow rates could result in elution volume errors, the flow rate, programmed by the automated gradient controller and monitored by a liquid flowmeter, was always kept at 1.0 mL/min. Both RI and UV (254 nm for PS) detectors were used for all the MW measurements.

Calibration curves were made by using narrow molecular weight PS standards (Polysciences) in the range of $M_w$ = 510-233 000. The value of the apparent peak molecular weight in all cases is

**Scheme I. General Strategies for the Synthesis of Macrocyclic AB Block Copolymers**



A=Styrene, B=$D_3$, $EX_2$=$Cl_2SiMe_2$, $I^-$ =$Li^+N^{\cdot-}$ or $Li^+$ $^-OCHCHO^-$ $^+Li$.

the average of at least three determinations. Molecular weights determined in this way were reproducible to within 2%.

**UV/Vis Spectroscopy.** UV/vis spectroscopy was used in the determination of the 1,4-dilithio-1,1,4,4-tetraphenylbutane carbanion concentration. Spectra were recorded on a Perkin-Elmer Lambda 6 UV/vis spectrometer with an Epson computer using a UV cell of 2-mm path length and a 1.9-mm spacer. The optical density measurements of the carbanion solutions were done under vacuum.

**Gas Chromatography.** Analysis of reagents by GC was performed on a Hewlett Packard 5890 GC equipped with a HP 3396 A integrator/printer for data manipulation, integration, and printing of data. An Alltech 50 m × 25 mm capillary column packed with poly(phenylmethylsiloxane) was used in this study while helium was the carrier gas. A gradient program was also applied to optimize separations.

**Nuclear Magnetic Resonance Spectroscopy.** Proton and $^{13}C$ NMR was performed on a Bruker Model AM-250 MHz FT-NMR, while $^{29}Si$ NMR was carried out on an IBM-Bruker 270-SY spectrometer. Proton NMR data were collected using 40 scans (acquisition time = 6 s; relaxation delay = 0 s). The $^{13}C$ and $^{29}Si$ NMR data were collected using 20 000 and 8000 scans, respectively. $^{13}C$ NMR spectra were run with broad-band proton decoupling. $^{29}Si$ NMR spectra were obtained by use of a heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 15 s. The $^{13}C$ and $^{29}Si$ NMR data were obtained on 10% and 20% solutions in $CDCl_3$. The proton NMR data were obtained on 5% solutions. $CDCl_3$ was utilized as an internal standard for proton and $^{13}C$ NMR, while $^{29}Si$ NMR spectra were externally referenced to TMS.

**Infrared Spectroscopy.** IR was used for the detection of SiOH groups of low-MW polymers. The spectra were recorded on a Nicolet 800 FT-IR spectrometer after the samples were incorporated into a KBr pellet.

## Results and Discussion

Three strategies for the synthesis of macrocyclic PS–PDMS block copolymers are illustrated in Scheme I. The first is the sequential anionic polymerizations of sytrene and $D_3$ by a difunctional initiator, such as lithium naphthalenide, for instance, followed by termination of the difunctional living copolymer with a large excess of DCDMS. The resulting Si–Cl functionalized polymer is subsequently coupled with a tetraphenylbutane dianion ($DD^{2-}$) at high dilution. This approach is attractive, at least in principle, since the reaction may be visually monitored due to the disappearance of the red color of the $DD^{2-}$. However, this attempt was unsuccessful due to the surprisingly slow rate of the coupling reaction. The second route requires the synthesis of both difunctional monodisperse PS and PDMS. After the living PDMS, prepared by initiation of $D_3$ with $LiOCH_2CH_2OLi$, is functionalized with an excess of DCDMS, it is reacted with living difunctional poly(styryllithium) at high dilution. In this case, the cyclization step has to be carried out at low temperatures in order to prevent side reactions of the PS anions.[13] This method proved impractical. The third strategy that was eventually followed involves sequential anionic polymerizations of styrene and $D_3$, followed by direct coupling with DCDMS at high dilution. Even though this strategy has the disadvantage in that there is no color change during the cyclization, the coupling rate is faster than those of the other methods. There appear to be no side reactions during this reaction.

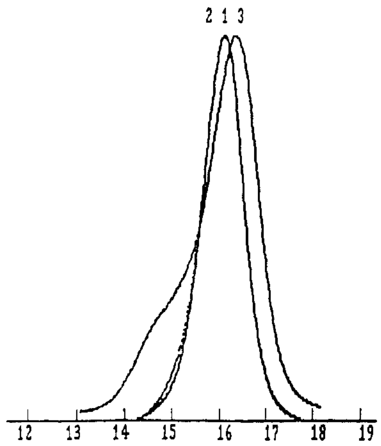
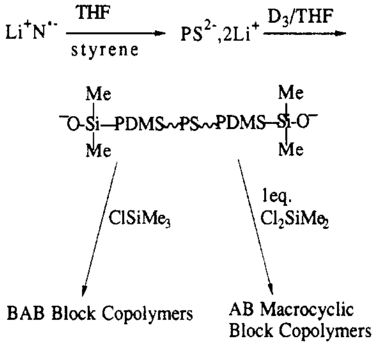


**Figure 3.** SEC chromatograms of unfractionated macrocyclic PS–PDMS (1) and the corresponding linear PDMS–PS–PDMS block copolymers (2) before and (3) after reaction with $Cl_2SiMe_2$.

**Scheme II. Synthesis of Macrocyclic PS–PDMS Block Copolymers and Their Linear BAB Precursors**



The synthesis of macrocyclic PS–PDMS block copolymers is shown in Scheme II and includes three steps. The first two steps involve the initiation/polymerization of styrene by lithium naphthalenide and the initiation/polymerization of $D_3$. The third step involves the cyclization of the living ends with DCDMS at high dilution.

The linear precursor ideally should be obtained under conditions where the polymer chains have stopped growing and the system is free of side reactions. This is readily achieved for the synthesis of low-MW copolymers. After polymerization of $D_3$ for 6.5 h, a substantial decrease in the apparent MW is observed upon cyclization while the MW of the uncyclized BAB living polymer remains at the original position as shown by SEC (Figure 3). This shows that isobaric linear and macrocyclic block copolymer pairs are produced.

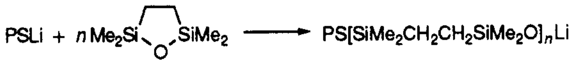
In the case of high-MW macrocycles, the MWDs of the linear precursors sometimes become broader or even bimodal. This is especially pronounced when the total MW of the block copolymer or of the PDMS block was

**Table I. Molecular Weights and Polydispersities of PS–PDMS Linear and Macrocyclic Block Copolymers As Determined by SEC**

| | PS | | | linear BAB[a] | | | macrocyclic AB | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| no. | $M_p$ | $M_w$ | $D$ | $M_p$ | $M_w$ | $D$ | $M_p$ | $M_w$ | $D$ | $\langle G\rangle$[b] | yield[c] |
| 426 | 2 280 | 2 300 | 1.11 | 2 810 | 2 900 | 1.10 | 2 210 | 2 570 | 1.08 | 0.79 | 76 |
| 423 | 2 420 | 2 410 | 1.08 | 3 410 | 3 660 | 1.09 | 2 640 | 3 420 | 1.13 | 0.77 | 83 |
| 625 | 3 100 | 3 040 | 1.06 | 4 550 | 4 510 | 1.16 | 3 600 | 4 230 | 1.11 | 0.79 | 82 |
| 726 | 4 330 | 4 830 | 1.18 | 5 930 | 7 030 | 1.20 | 4 950 | 7 490 | | 0.83 | 87 |
| 419 | 6 200 | 6 400 | 1.13 | 9 280 | 10 410 | 1.14 | 7 200 | 8 320 | 1.13 | 0.77 | 86 |
| 422 | 6 880 | 7 090 | 1.11 | 11 610 | 12 430 | 1.09 | 9 420 | 9 810 | 1.07 | 0.81 | 79 |
| 929 | 11 900 | 14 800 | 1.21 | 20 830 | 27 770 | 1.24 | 14 410 | 19 180 | 1.29 | 0.69 | 70 |
| 104 | 21 100 | 22 830 | 1.08 | 25 220 | 35 650 | 1.29 | 18 770 | 20 240 | 1.14 | 0.74 | 57 |
| 1024 | 39 180 | 35 880 | 1.15 | 57 800 | 73 150 | 1.22 | 40 950 | 47 110 | 1.17 | 0.71 | 50 |
| 312 | 53 570 | 50 520 | 1.03 | 57 750 | 59 620 | 1.03 | 49 210 | 49 010 | 1.07 | 0.85 | 80 |
| 316 | 23 090 | 22 330 | 1.03 | 79 820 | 86 810 | 1.10 | 69 780 | 81 330 | 1.12 | 0.87 | 64 |

[a] PDMS–PS–PDMS. [b] $\langle G\rangle = M_{pc}/M_{pl}$. [c] Approximate cyclization yield (%) estimated from SEC. [d] Unfractionated macrocyclic block copolymer.

large ($M \geq 25\,000$), the polymerization time of $D_3$ was long, or the initiator concentration was high. Such side reactions are probably due to the following reasons: (1) a coupling reaction involving two PS anions,[13] (2) chain redistribution reactions during the polymerization of $D_3$,[14] and (3) two propagating and slowly interconverting sites at different degrees of aggregation during the polymerization of $D_3$.[15] Thus the polymerization has to be stopped before propagation is completed and the side reactions become important. The details will be discussed in a separate paper. We have found that the slow initiation of $D_3$ by PSLi may be avoided by the use of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (EDS)[16] for the end-capping reaction:



$$\mathrm{PSLi} + n\,\mathrm{Me_2Si\overset{\frown}{\ \ }SiMe_2(O)} \longrightarrow \mathrm{PS[SiMe_2CH_2CH_2SiMe_2O]_{\mathit{n}}Li} \quad (1)$$

This is then followed by addition of the required amount of $D_3$ which is polymerized rapidly by the end-capped polystyrene.

It should be pointed out that the high-MW shoulder, which is a side reaction product of the linear living PDMS–PS–PDMS precursors, does not contaminate the fractionated macrocycle, since after fractionation this side product remains in the high-MW fraction along with other polycondensate products.

Based on the above synthetic strategy, a series of macrocyclic PS–PDMS block copolymers with precursor MWs ranging from 2800 to 80 000 were prepared (Table I). In each run, both living PS and living PDMS–PS–PDMS precursors were isolated and terminated with methanol (for PS) or TMSCl (for living BAB). The isobaric BAB linear precursors are reference samples for the macrocyclic block copolymers and also serve as comparison samples for the study of structure/property relationships. The exact molecular weight of the macrocyclic block copolymer is of course the same as that of the linear precursor, except for a small increase of 89 D for the linear precursor terminated by TMSCl. This increase is, however, obviously insignificant especially at high MW.

Large reaction flasks (1000 mL) were used in order to keep silanolate concentrations low during polymerization and coupling. The low anion concentrations tend to minimize silanolate aggregation.[17] Alternatively, larger quantities of precursor polymers (6–10 g) could be prepared than would be possible with the smaller flask (250 mL) used earlier.[11] Judging by the excellent cyclization yields (from SEC, Table I), we infer that the concentration of cyclization chains is rather low (about $10^{-6}$ M) as calculated from the Jacobson–Stockmayer equation.[18] This low concentration is possible due to the slow rate of addition of the polymer dianion during the cyclization step which in turn is possible because of the excellent thermal ability of the silanolates. As expected, the cyclization yield generally decreases with increasing copolymer molecular weight.[18]

Evidence for the formation of macrocycles is provided by SEC. Upon cyclization there is a clear decrease in the apparent MW of the macrocycle due to the smaller hydrodynamic volume of the cyclic polymer. The $\langle G\rangle$ values, defined as the ratio of the apparent peak MW of cyclic and linear polymers ($\langle G\rangle = M_{pc}/M_{pl}$), are listed in Table I and range from 0.69 to 0.87 over the MW range of 2800–80 000. With the exception of samples 312 and 316 (see below), Table I shows a small increase in $\langle G\rangle$ as the molecular weights decrease below about $6 \times 10^3$ Da. A similar change, observed for the PS and poly(2-vinylpyridine) macrocycles, was attributed to a decrease in the chain flexibility at low DPs.[19]

The higher $\langle G\rangle$ values for high-MW macrocycles (samples 312 and 316) are probably due to the increase in MW of the portion of the living BAB precursor that was inadvertently allowed to continue polymerizing until well after the completion of the coupling action.

**NMR and FTIR Studies.** In addition to SEC, the low-MW linear and macrocyclic block copolymers were characterized by NMR. Linear and macrocyclic low molecular weight samples 426 (Table I) contain a PS block ($M = 2300$) and about two $D_3$ units. The proton NMR results confirm that both PS and PDMS blocks are incorporated into the block copolymer. In the PDMS region of the macrocycle, there is appreciable peak broadening compared to the linear block copolymer. Since the sample pairs have the same MW and chemical composition, this result can only be due to the difference in chain topology. Similar behavior was observed by Gibson et al. for low-MW linear and cyclic PS, prepared by coupling with DCDMS.[20]

Since the $^1$H NMR absorptions in the PDMS region are overlapped, making assignments difficult, the paired samples were analyzed by $^{13}$C NMR. Figure 4 shows the $^{13}$C spectrum of the short PDMS section. There are three distinct peaks (1.82, 1.19, and 1.08 ppm) for the linear samples, while a single peak (1.11 ppm) is present in the macrocyclic (Table II). This is reasonable since the linear sample contains both trimethylsilyl chain ends (M) and dimethylsiloxy repeat units (D and M′), whereas the cyclic sample only has $(SiMe_2O)_n$ repeat units. This assumption is also in good agreement with the model compound studies. Hexamethyldisiloxane (HMDS), a model compound for the polymer chain end, exhibits a chemical shift (1.97 ppm) similar to that of the trimethylsilyl chain end (1.82 ppm). On the other hand, the cyclic $D_3$ monomer has a chemical

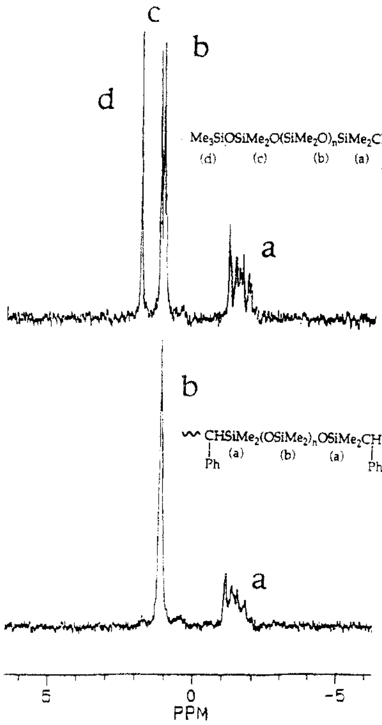


**Figure 4.** $^{13}C$ NMR spectra (sample 426) of linear and macrocyclic PS–PDMS block copolymers.

**Table II.** $^{13}C$ **NMR Results of Linear and Macrocyclic Block Copolymers**[a]

| sample | chemical shift (ppm) | |
|---|---|---|
| | M | D (M′) |
| 426 linear | 1.82 | 1.08 (1.19) |
| 426 cyclic | | 1.11 |
| $D_3$ | | 0.90 |
| HMDS | 1.97 | |

[a] $\underset{M}{(CH_3)_3SiO}\underset{D}{(CH_3)_2SiO}\underset{D'}{(CH_3)_2SiO}\underset{M'}{(CH_3)_2Si}CH(Ph)CH_2\text{–PS}$.

**Table III.** $^{29}Si$ **NMR Results of Linear and Macrocyclic Block Copolymers**

| sample[a] | chemical shift (ppm) | | | | |
|---|---|---|---|---|---|
| | M | M′ | SiCl | SiOH | D |
| 426 cyclic | | 5.02 | | | -21.2, -21.9 |
| 426 linear | 7.38 | 4.99 | | | -21.0, -21.5 |
| A | | | | -13.6 | -23.9 |
| B | | | 1.4 | | -20.8, -23.0 |
| C | 7.1 | | | | -21.6, -22.4 |

[a] A = $HOSi(CH_3)_2O[Si(CH_3)_2O]_2Si(CH_3)_2OH$. B = $ClSi(CH_3)_2O[Si(CH_3)_2O]_3Si(CH_3)_2Cl$. C = $(CH_3)_3SiOSi(CH_3)_2O[Si(CH_3)_2O]Si(CH_3)_2OSi(CH_3)_3$.

shift (0.90 ppm) similar to that of the repeat units (1.11 ppm).

Larger chemical shift differences are observed for the $^{29}Si$ NMR of the macrocyclic and linear polymers (Table III). The change in chemical shift between the chain end (M) and the repeat unit (D) of the linear polymer is almost 30 ppm, and the difference between the chain end (M) and the silicon (M′) connected directly to the PS chain is about 2.4 ppm. Moreover, no chain end was detected in the cycle, although the linear sample clearly indicates the existence of the polymer chain end at 7.38 ppm.[21]

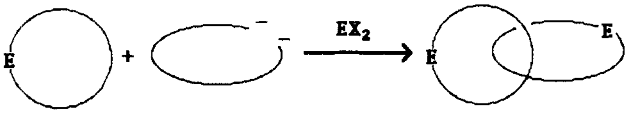
If the macrocyclic product were contaminated with linear polymer produced during cyclization by DCDMS, the Si–OH bond (due to the hydrolysis of the Si–Cl bond or termination of silanolate by water) could be present. However, no Si–OH or Si–Cl was observed by $^{29}Si$ or $^1H$ NMR. Furthermore, FTIR measurements show the absence of the Si–OH bond (3600 $cm^{-1}$ for free OH; 3400–3200 $cm^{-1}$ for hydrogen-bonded OH) in the macrocyclic block copolymer. Of course, the formation of Si–O–Si bonds from the reaction of Si–OH with Si–Cl bonds is a possibility. However, intra- or intermolecular bond formation of this type would yield macrocycles or higher MW products. This is of course not a problem as these reactions merely duplicate the intended outcome of the coupling reaction.

**Table IV. Block Copolymer Compositions As Measured by SEC and NMR**

| | linear BAB | | | | |
|---|---|---|---|---|---|
| | | | PDMS % | | |
| no. | $M_p$ | $D$ | SEC[a,b] | NMR[b] | macrocyclic AB: PDMS % NMR |
| 426 | 2810 | 1.10 | 18.9 | 17.2 | 19.3 |
| 423 | 3410 | 1.09 | 29.0 | 25.0 | |
| 625 | 4550 | 1.16 | 31.9 | 28.7 | |
| 419 | 6200 | 1.13 | 33.2 | 23.3 | |
| 422 | 11610 | 1.09 | 40.7 | 42.6 | 39.0 |
| 312 | 57750 | 1.03 | 7.2 | 5.2 | |
| 316 | 79820 | 1.10 | 71.1 | 73.3 | |

[a] Polystyrene standards. [b] Averaged value of three runs.

**Scheme III. Formation of Catenated Polymers**



Block copolymer compositions were determined by both SEC and NMR (Table IV). The small differences between them are probably due to the fact that the SEC MWs based on polystyrene calibration would be subjected to errors since the hydrodynamic volume of the PDMS block differs from that of the PS of the same MW in THF. The NMR measurements, however, should give a more accurate block ratio.

The formation of catenated or knotted polymers is a potential problem in the synthesis of polymer macrocycles. The formation of catenates involves the "coupling" of two macrocycles (Scheme III). As a result, the apparent MW of the product is roughly doubled. Higher molecular weight cycles are possible because of catenation involving higher MW macrocycles and/or precursors. In that respect, catenation has a similar effect as "polycondensation", in that the ABA precursors are "coupled" together (Scheme III). Thus, catenation products in principle would be difficult to distinguish from "polycondensates". The absence of higher MW shoulders in the fractionated product at least indicates their absence in the purified macrocycles.

The presence of the knotted polymers in the purified macrocycles is also unlikely due to the following reasons. First, the cyclization was carried out in a good solvent (THF), so that the polymer chain should expand, reducing polymer chain folding. Second, the MW range in this study may not be high enough for knot formation. Roovers concluded that the possibility for the formation of knotted polymers is very small when the polymer MW is less than a few hundred thousand.[22] Third, the hydrodynamic volume upon knot formation should decrease. Thus, a low-MW shoulder should be observed in the crude cyclization product. However, no low-MW shoulder was detected.

In conclusion, the SEC results, along with NMR and FTIR data, strongly support the formation of uncontaminated monodisperse macrocyclic block copolymers.

**Synthesis of Macrocyclic PS–PEDS–PDMS–PEDS (ABCB) Tetrablock Copolymer.** As indicated earlier,

**Table V. Apparent Molecular Weights and Polydispersities of PS-PEDS-PDMS Linear and Macrocyclic Block Copolymers**

| | $M_p$ | $D$ | PS % | PEDS % | PDMS % | $G$ |
|---|---|---|---|---|---|---|
| PS 817 | 14,580 | 1.03 | | | | |
| linear BAB | 19,550 | 1.11 | 74.6 | 25.4 | | |
| linear CBABC | 41,540 | 1.24 | 35.1 | 12.0 | 52.9 | |
| cyclic ABC | 32,580 | 1.23 | 35.1 | 12.0 | 52.9 | .78 |

2,2,5,5-tetramethyl-2,5-disila-1-oxycyclopentane (EDS) reacts efficiently with PS anions at low temperatures ($<-20$ °C). The resulting silanolate anion quantitatively initiates $D_3$. Therefore, a pentablock copolymer, PDMS-PEDS-PS-PEDS-PDMS, may be synthesized in THF through sequential anionic polymerization. The living polymers from such a reaction at different stages were isolated from the reaction mixture and analyzed by SEC. The increases in the apparent MW from PS to PEDS-PS-PEDS to PDMS-PEDS-PS-PEDS-PDMS indicate the formations of the triblock and pentablock copolymers. Moreover, the MWDs of these precursors are narrow, suggesting that the copolymerization is largely free of side reactions. The presence of PS, PEDS, and PDMS blocks is also confirmed by $^1$H NMR. Thus, in addition to the peaks due to PS and PDMS, the $CH_2$ peak of the EDS fragment ($SiMe_2CH_2CH_2SiMe_2-$) absorbs at 0.38 ppm.

The linear pentablock copolymer precursor anion was cyclized at high dilution. As expected, upon cyclization a decrease in the apparent peak MW was observed, indicating the formation of the macrocyclic ABCB tetrablock copolymer. This copolymer was fractionated in a manner similar to that described before. The results are listed in Table V. Since the synthesis involves a high-MW macrocyclic block copolymer, the cyclization yield is relatively low (<50%).

The properties of these and other macrocyclic block copolymers are the subject of further studies by this group.

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