# Synthesis and Characterization of Well-Defined Poly(α-methylstyrene)-*b*-poly(dimethylsiloxane) Block Copolymers

**James Lee and Thieo E. Hogen-Esch***

*Loker Hydrocarbon Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661*

*Received August 17, 2000; Revised Manuscript Received January 4, 2001*

ABSTRACT: The anionic synthesis is reported for AB and ABA narrow distribution block copolymers of poly(α-methylstyrene) (PAMS, A) and poly(dimethylsiloxane) (PDMS, B) with molecular weights ranging between $8.2 \times 10^3$ and $1.9 \times 10^5$. In one approach living PAMS end-capped with a short polystyrene block (PAMS−PSLi) was obtained by the *tert*-butyllithium initiated polymerization of AMS in THF at −78 °C followed by the sequential addition of styrene, 2−3 equiv of 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (EDS) at −20 °C, and hexamethylcyclotrisiloxane ($D_3$) at 25 °C. A more convenient synthesis without the use of styrene is the direct end-capping of living PAMSLi with EDS at −10 °C followed by the polymerization of $D_3$ at 25 °C. The living block copolymers were then end-capped with $Me_3SiCl$ or coupled with $Me_2SiCl_2$ to give matching AB and ABA narrow distribution block copolymers. The glass transition temperatures of the PAMS blocks were at least 10 °C higher than that of the PAMS−PS blocks.

## Introduction

Block copolymers of poly(α-methylstyrene) and poly(dimethylsiloxane) (PAMS-*b*-PDMS)[1−3] are of interest as thermoplastic elastomers with enhanced thermal stability because of the high glass transition temperatures of PAMS ($T_g = 177$ °C for molecular weights above 60 000).[4−6] Although the anionic "living" homopolymerization of α-methylstyrene (AMS)[11−15] and that of hexamethylcyclotrisiloxane ($D_3$)[12−18] has been studied extensively, the corresponding synthesis of narrow molecular weight distribution (MWD) PAMS-*b*-PDMS, at least to our knowledge, has not been reported.

The synthesis of PAMS−PDMS block copolymers should start with the anionic polymerization of AMS using a monofunctional initiator such as *n*-butyllithium or *tert*-butyllithium or a "difunctional" initiator, such as sodium or lithium naphthalide, in THF at −78 °C. These polymerizations give narrow MWD PAMS with typical $D$ values of 1.04−1.25.[4,10,11]

Narrow MWD PDMS with a $D$ value of less than 1.25 may be synthesized at ambient temperature by initiation of $D_3$ with an alkyllithium, lithium alkoxides, or lithium silanolates in nonpolar solvents such as toluene, hexane, or benzene or their mixtures with DMSO[13,14] and THF.[15,16] The presence of lithium as counterion generally is required in order to minimize side reactions.[12] Because of its high basicity, the PAMS anion should be an effective initiator for $D_3$. However, such a synthesis presents several difficulties, including (a) the low ceiling temperature of PAMS ($T_c$ for neat monomer is 61 °C),[7,8] (b) the tendency of the PAMS anion toward side reactions at ambient temperatures, and (c) the generally low reactivity of delocalized carbanions toward $D_3$ in THF and similar solvents.[19,20] Even the less sterically hindered polystyryllithium (PSLi) in THF reacts relatively slowly with $D_3$, even at −20 °C.[19] Thus, the crossover reaction converting PAMS to an effective macroinitiator of $D_3$ polymerization presents a challenge.

The first synthesis of PAMS−PDMS was carried out by Saam by anionic polymerization of AMS in THF at −70 °C, followed by addition of styrene to end-cap the PAMS anion in order to avoid depolymerization of AMS.[1] Warming to 25 °C and addition of $D_3$ led to the formation of the corresponding block copolymer of which the MWD was not reported. Presumably due to the relatively high content (20%) of polystyrene, the hard block had a glass transition temperature ($T_g$) of only approximately 126 °C[1] as compared to a $T_g$ of 145 °C for homo-PAMS of similar molecular weight.

Here we report our attempt to extend our previous synthesis of PS−PDMS[19] to the synthesis of narrow MW distribution PAMS-*b*-PDMS by a simpler procedure that eliminates the use of styrene as a comonomer. This procedure involves the sequential anionic polymerization of AMS, followed by the end-capping of 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (EDS) and addition of $D_3$ to give a narrow MWD PAMS−PDMS (Scheme 1).

## Experimental Section

**Materials.** AMS (Aldrich, 99%) was first dried over $CaH_2$ under argon and then stirred over *tert*-butyllithium. After a dark red color appeared the monomer was vacuum-distilled into ampules. Styrene (Aldrich, 99%) was first dried over $CaH_2$ and then purified over potassium mirrors as described elsewhere.[19] *tert*-Butyllithium (Aldrich) was carefully purified by sublimation in vacuo. This purification was crucial because commercially available *tert*-butyllithium usually contains lithium alkoxides and similar impurities that are inactive toward AMS but are capable of initiating $D_3$. Monomers $D_3$ (Petrarch, 99%) and 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (EDS, Petrarch, 98%), $Me_2SiCl_2$ (Aldrich, 99%), and $Me_3SiCl$ (Aldrich, 99%) were purified by stirring over $CaH_2$ followed by distillation onto fresh $CaH_2$ and vacuum distillation into ampules.

**Polymerizations** were carried out under high vacuum ($10^{-5}$−$10^{-6}$ Torr) as reported elsewhere.[19] Thus, PAMSLi (Table 2) was synthesized by slow distillation of about 5 g of AMS ($4.3 \times 10^{-2}$ mol) into a rapidly stirred solution of *t*-BuLi ($7.5 \times 10^{-4}$ mol) in 30 mL of THF dissolved in 5 mL of THF was added to the solution. The thermodynamics of polymerization of AMS is well-known ($\Delta H$ and $\Delta S$ are −35.1 kJ/mol and −104 J/mol$^{-1}$ K$^{-1}$, respectively)[6] so that the equilibrium

10.1021/ma001452z CCC: $20.00

**Scheme 1. Synthesis of PAMS−PDMS AB and ABA via Anionic Polymerization through End-Capping with EDS**

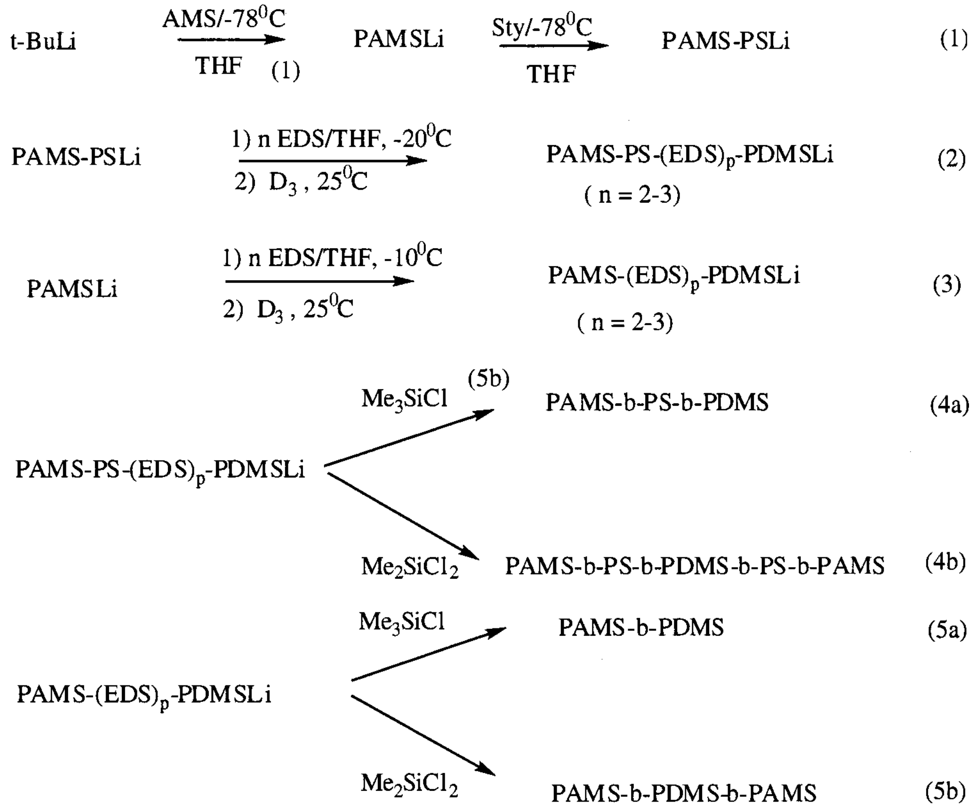


**Table 1. Compositions, Molecular Weights, and MW Distributions of PAMS−PS-*b*-EDS−PDMS (AB) and PAMS−PS-*b*-EDS−PDMS−EDS-*b*-PS−PAMS (ABA) Copolymers**[a]

| | $M_n \times 10^3$ [a] | $D$ | $M_n \times 10^3$ [b] | PS[b] (wt %) | PDMS (wt %)[b] | conversion D$_3$ (%) |
|---|---|---|---|---|---|---|
| PAMS−PS(1) | 48.0 | 1.25 | | 9 | | |
| AB11 | 81.0 | 1.20 | 75.0 | | 36 | 45 |
| AB12 | 150 | 1.24 | 192 | | 75 | 85 |
| PAMS−PS(2) | 46.4 | 1.25 | | 13 | | |
| AB21 | 65.0 | 1.24 | 64.0 | | 28 | 38 |
| PAMS(3) | 27.0 | 1.08 | | | | |
| PAMS(3)−PS | 29.0 | 1.14 | | 15 | | |
| AB31 | 107 | 1.07 | 93.5 | | 69 | 63 |
| AB32 | 72.0 | 1.05 | 70.7 | | 59 | 40 |
| AB33 | 109 | 1.22 | 132 | | 78 | 95 |
| ABA31 | 190 | 1.28 | 207 | | 72 | 67 |
| ABA32 | 134 | 1.20 | 157 | | 63 | 44 |

[a] A and B refer to PAMS and PDMS, respectively. SEC using polystyrene standards. [b] $M_n$ values of PAMS−PS copolymers based on proton NMR integration of PAMS (PAMS−PS) and PDMS (PDM−EDS) resonances (see text). All PDMS block copolymers contain 2−3 EDS units.

**Table 2. PAMS-*b*-PDMS (AB) and PAMS-*b*-PDMS−PAMS (ABA) Copolymers Synthesized by Initiation with PAMS−EDSLi**[a,b]

| sample | $M_n \times 10^3$ | $D$ | $M_n \times 10^3$ | PDMS (wt %)[b] | conversion D$_3$ (%)[c] |
|---|---|---|---|---|---|
| PAMS | 5.2 | 1.17 | | | |
| AB1 | 11.0 | 1.16 | 14.8 | 65 | 16 |
| AB2 | 30.0 | 1.09 | 23.6 | 78 | 42 |
| AB3 | 8.2 | 1.20 | 9.8 | 47 | 8 |
| AB4 | 12.0 | 1.16 | 13.3 | 61 | 13 |
| AB5 | 33.0 | 1.14 | 30.6 | 83 | 33 |
| ABA1 | 26.0 | 1.13 | 34.6 | 70 | 18 |
| ABA2 | 56.0 | 1.11 | 57.8 | 82 | 42 |

[a] A and B refer to PAMS and PDMS, respectively. $[D_3]_0 = 0.5-1.0$ M. MW's by SEC using polystyrene standards. [b] PDMS content and copolymer block $M_n$ is based on $^1$H NMR of copolymers and SEC of PAMS. All PDMS block copolymers contain 2−3 EDS units

concentration of AMS at various temperatures may be calculated. Upon addition of 304 mg (2.5 equiv/chain) of EDS the red color of the PAMSLi disappeared over a few minutes, indicating the ring opening of the EDS, to give a stable PAMS−EDSLi precursor solution that was divided into several ampules and could be stored for extended periods at −20 °C (Scheme 1). The AMS polymerization yield at −10 °C was about 80%.

As shown in Table 1 in some cases styrene (about 40−60 equiv with respect to initiator) was distilled into the polymer solution until its color was changed from deep red to orange, indicating the conversion of PAMS anion to the PAMS−PS anion. Upon addition of 2−4 equiv of EDS to this PAMS−PSLi at −20 °C, the orange color of the PSLi disappeared with the formation of PAMS−PS−EDSLi.

The synthesis of the block copolymers was carried out by addition of D$_3$ (B block) to the PAMS−EDSLi or PAMS−PS−EDSLi solutions. For instance, 6 g ($2.7 \times 10^{-2}$ mol) of D$_3$ dissolved in 5 mL of THF was added to 50 mL of a THF solution of 400 mg of PAMS−EDSLi precursors (A block, $1 \times 10^{-4}$ mol, Table 2) at ambient temperatures. Following the partial polymerization of D$_3$ (33% conversion of D$_3$; see Table 2, AB5) the PAMS−PDMSLi solution was terminated with Me$_3$SiCl. Precipitation into methanol gave 2.2 g of copoloymer. In other cases (Table 1, AB31 and AB 32; Table 2, AB1 and AB2) two portions of the same PAMS−PS−EDS−PDMSLi or PAMS−EDS−PDMSLi solutions were terminated with Me$_3$SiCl and coupled with Me$_2$SiCl$_2$ in order to produce the matching (equal composition) AB or ABA block copolymers. During the D$_3$ polymerizations and the subsequent coupling reactions, solution aliquots were withdrawn for direct SEC analysis of the polymeric silanolates in order to monitor the reaction progress. The block copolymers were precipitated by addition of solutions of the terminated or coupled polymers into excess methanol followed by washing with methanol. Samples were dried in a vacuum oven at 60 °C for 3 days.

PAMS−PS block copolymer compositions were determined by isolation and protonation of a small sample of the PAMS-*b*-PSLi followed by $^1$H NMR integration of the groups of

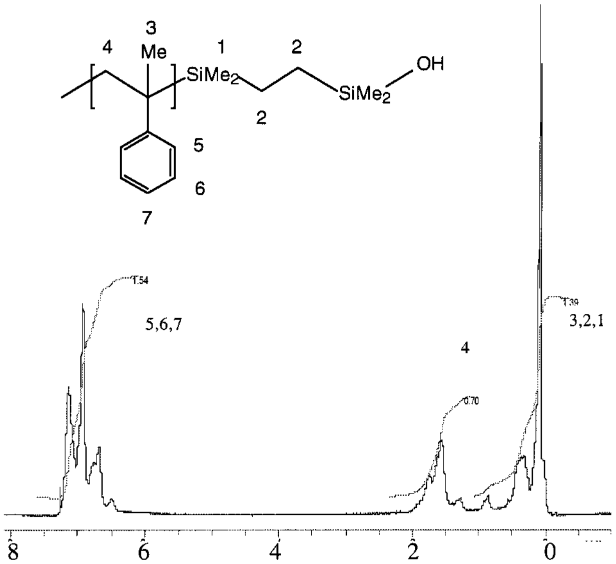


**Figure 1.** Proton NMR (250 MHz) spectrum of EDS end-capped PAMS in $CDCl_3$ (Table 2).

resonances at 0.0−1.08 ppm (corresponding to absorptions of the syndiotactic to isotactic α-methyl protons of PAMS, respectively)[21] and 1.1−2.2 ppm (methylene protons of PAMS and methylene and methine protons of PS). The PAMS−EDS, PAMS−EDS−PDMS, PAMS−PS−EDS, or PAMS−PS−EDS−PDMS block copolymer compositions were determined by $^1$H NMR integration of the methyl protons of PDMS and EDS at about 0.0 ppm, the methylene protons of EDS at 0.4 ppm, the α-methyl protons of PAMS at 0−1.05 ppm, the methylene protons of PAMS and PS at 1.1−2.2 ppm, and aromatic protons at 6.4−7.4 ppm (Figure 1). The very small blocks of PEDS (about 2−3 equiv/chain) were integrated as a part of PDMS.

**Characterization.** Proton and $^{13}$C NMR were performed on a Bruker model AM-250 MHz FT-NMR. The $^1$H NMR analyses were carried out with 5 wt % solutions in $CDCl_3$ while the $^{13}$C NMR spectra were obtained with 10−15 wt % solutions. SEC analysis was carried out at 25 °C in THF for the case of the PAMS precursors and in toluene for the PAMS−PDMS block copolymers at a flow rate of 1.0 mL /min on a “Waters” high-pressure liquid chromatography system consisting of a 510 HPLC pump, a UK6 injector, a 2 $\mu$m precolumn filter and 500 and $10^4$ Å (10 $\mu$m) “Ultrastyragel” columns and a model 410 refractive index detector, a liquid flow meter, and a PC interface for data collection. Calibration was carried out with PS standards (Polysciences). The injected sample concentrations were 0.2 wt % for samples of molecular weight above 25 000 and 0.5 wt % for samples of molecular weight under 25 000 with toluene as eluting solvent. Elution volumes of PS and PAMS were essentially the same for molecular weights ranging from $4 \times 10^4$ to $1.2 \times 10^5$. Thus, polystyrene calibration gives a good approximation of PAMS MW’s.[7,8] The compositions and $M_n$ values of PAMS−PS−PDMS or PAMS−PDMS were calculated on the basis of proton integration ratios of PAMS−PS or PAMS to EDS−PDMS and the molecular weights of PAMS−PS or PAMS measured by SEC. Molecular weight distributions of PAMS−PS−PDMS and PAMS−PDMS were also analyzed by SEC. Glass transition temperatures were measured by differential scanning calorimetry (DSC) using a V4.0 Dupont 2000 unit with a heating rate of 10 °C/min from room temperature to 200 °C and under nitrogen gas. The glass transition zone was defined as the temperature range between two intersection points of the baselines with the extrapolated sloping portion of the DSC curves, the value of the $T_g$ being defined as the midpoint of the heat capacity change.

## Results

A purchased PAMS−PS−PDMS sample from Dow (presumably synthesized by Saam’s method[1]) had a relatively wide MWD ($D = 1.51$). This is consistent with the following: (a) slow initiation of $D_3$ by PAMS−PSLi, (b) competing hydride elimination and protonation by THF of the benzylic anions,[22−25] (c) lithium silanolate redistribution reactions and/or lithium silanolate aggregation during the $D_3$ polymerizations (Scheme 2).[11,27]

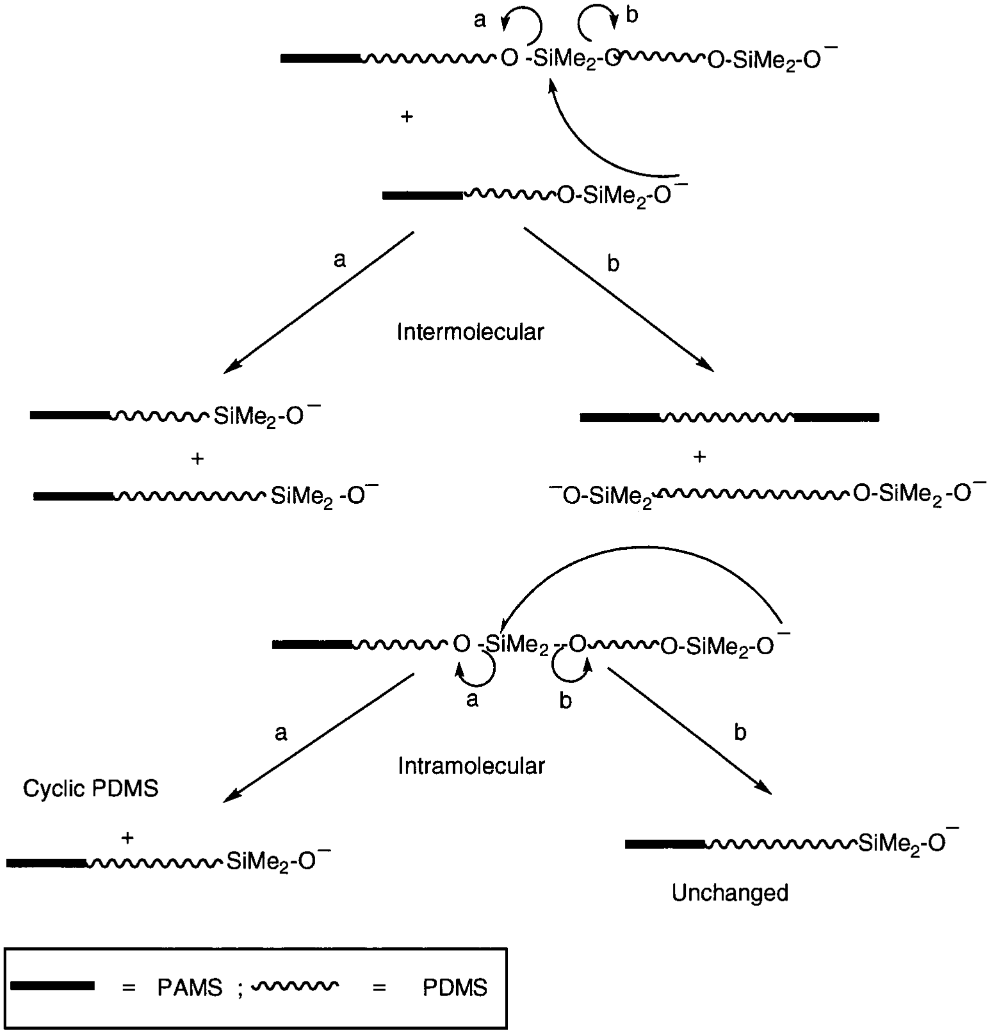
**Synthesis of PAMS(A)−PS−EDS-*b*-PDMS(B) Block Copolymers.** It was previously reported that living PSLi at −20 °C may be reacted quantitatively with EDS[27] (which is more reactive than $D_3$) to give a lithium silanolate that is capable of initiating $D_3$ producing narrow distribution PAMS-*b*-PDMS (AB) and PS-*b*-PDMS-*b*-PAMS (ABA) block copolymers. The reaction of $D_3$ with PAMSLi at −20 °C in THF was too slow to be practical. However, upon addition of styrene the resulting PAMS−PSLi anion could be reacted with 2−3 equiv of EDS to produce the corresponding PAMS−PS−EDSLi silanolate precursor (Scheme 1).

In the synthesis of PAMS−PSLi, styrene was slowly distilled into the red $PAMS^-$ solution until the red color of the solution changed to orange, indicating conversion to the PS anion. Nonetheless, a large molar excess of styrene (40−60 equiv) was needed for the color change. Even so, the color sometimes reversed from orange to red. Furthermore, the SEC chromatograms of the PAMS−PS samples resulted in a pronounced low molecular weight shoulder (Figure 2). Similar results were obtained by Yu et al.,[30] who, in studying the addition of styrene to PAMS anion, noticed a color change from deep red to yellow (characteristic of the styryl anion) followed after 10 min by the reappearance of the deep red color of the PAMS anion. Thus, for the above cases styrene is a rather inefficient end-capping agent. This could occur if the addition of styrene to PSLi is much faster than the reaction of the PAMS anion with styrene, thus leaving some of the PAMSLi unreacted.[28] Furthermore, the PAMSLi is in equilibrium with AMS which, being less reactive than styrene, end-caps the PSLi consistent with the color from orange to red.

Upon addition of EDS to the PAMS−PSLi polymer precursor, the anion reacted with EDS, but a residual faint red color remained visible typical of the PAMS anion, again indicating that the PAMS anion did not react completely with styrene. As a result, it was necessary to use a fairly large styrene concentration (40−60 equiv) of styrene with respect to initiator

As shown in Figure 2, the PAMS precursor (Table 1, no. 3) with a *D* value of 1.08 has no low molecular weight shoulder whereas PAMS−PS with a PS content of 15 wt % has a low molecular weight shoulder with a *D* value of 1.14. However, once capped with EDS, this precursor was kept at −20 °C for weeks without showing signs of redistribution or other side reactions and was capable at ambient conditions of initiating $D_3$ to give narrow MWD PAMS−PS−PDMS block copolymers (Table 1). The synthesis of “matching” (same composition) PAMS-*b*-PDMS (AB) and PAMS-*b*-PDMS-*b*-PAMS (ABA) block copolymers was carried out by reaction of two portions of the same precursor solution of PAMS−PS−EDS-*b*-PDMSLi or PAMS−EDS-*b*-PDMSLi with $Me_3SiCl$ and $Me_2SiCl_2$, respectively (Scheme 1, eqs 4a and 4b). Successful coupling is achieved when the ABA block copolymer had doubled its number-average MW compared to the corresponding AB block without the presence of low MW shoulders, indicating the presence of precursor. In this case, the polymerization reactions of $D_3$ and the coupling of the resulting living block

**Scheme 2. Inter- and Intramolecular Redistribution Reactions of PAMSLi and Similar Living Block Copolymers**



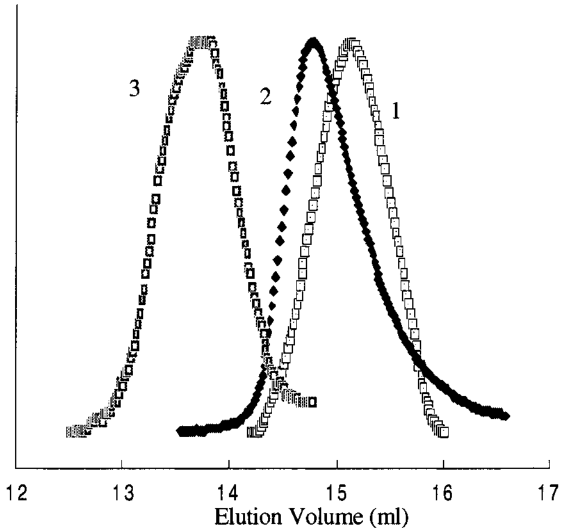


**Figure 2.** SEC chromatograms of samples of Table 1. PAMS-(3)) (curve 1), oligo-styrene end-capped PAMS(3)−PS (curve 2), and PAMS−PS-EDS-*b*-PDMS AB31 (curve 3).

copolymers could be followed by direct SEC analysis of the reaction solution as the reaction progressed.[31] The AB and ABA block copolymers synthesized by this route had masses between 65K and 190K with molecular weight distributions ($D = M_w/M_n$) ranging between 1.05 and 1.28 (Table 1). Coupling is seen to be quantitative within experimental error, and no shoulders were observed corresponding to the precursor anions in most cases. As shown in Table 1, sample AB33 had wider distributions ($D > 1.20$) compared to its PAMS−PS precursor ($D = 1.14$). In this case side reactions in the polymerization of $D_3$ may have occurred, as polymer chains and polymerization times were long while $D_3$ conversions were high at 95%. The somewhat broadened MWD ($D = 1.28$) of copolymer ABA31 compared to that of its corresponding AB31 precursor ($D = 1.07$) is most likely due to an inadvertent excess of $Me_2SiCl_2$, resulting in the formation of uncoupled and $Me_2SiCl$ end-functionalized product and not to unreacted precursor anion, since it did not disappear on further addition of $Me_2SiCl_2$. Agreement between number-average MW's determined by SEC and NMR was acceptable given the lower accuracy of the $M_n$ determinations by proton NMR.

**Synthesis of PAMS−EDS-*b*-PDMS AB and ABA Block Copolymers.** Although the PAMS anion was less reactive than that of PS, we found that it readily and completely reacted with EDS at −10 °C (Scheme 1, eq 4). Under these conditions addition of EDS and $D_3$ resulted in the formation of narrow distribution PAMS-*b*-PDMSLi. Once reacted with EDS, the resulting end-capped PAMS−EDSLi, like the PAMS−PS−EDSLi silanolates, could be stored for extended periods at −20 °C and were effective initiators for the polymerization

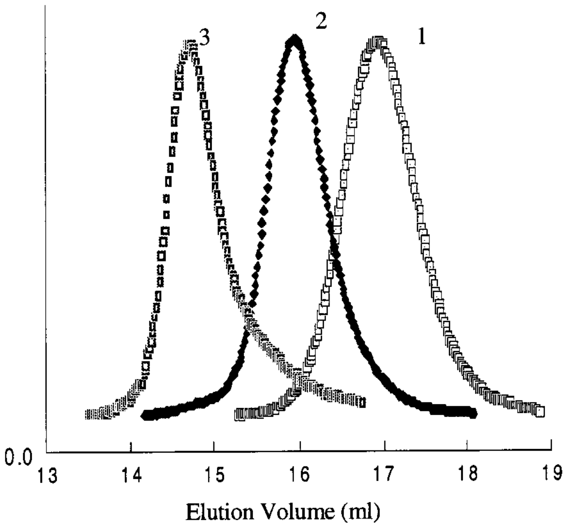


**Figure 3.** SEC chromatograms of PAMS and copolymers of Table 2. PAMS (curve 1); PAMS−EDS-*b*-PDMS, AB1 (curve 2) and PAMS−EDS-*b*-PDMS, AB5 (curve 3).

**Table 3. Glass Transition Temperatures of Several PAMS and PAMS−PS Precursors**

| sample | $M_n \times 10^3$ | $T_g$ (°C) |
|---|---|---|
| PAMS (ref 6) | 64.0 | 177 |
| PAMS (ref 11) | 7.0[b] | 145 |
| PAMS (ref 11) | 31.0[b] | 155 |
| Table 1, PAMS−PS(3) | 29.0 | 134 |
| Table 1, PAMS−PS(3)-EDS | 29.3[a] | 132 |
| Table 2, PAMS | 5.2 | 138 |
| Table 2, PAMS-EDS | 5.5[a] | 135 |
| PAMS−PS (ref 1) | 8.0 | 126 |

[a] A mass of 320 is added to the masses of the precursor polymers to account for the small (2−3 equiv/chain) amount of EDS added. [b] Weight-average MW reported only.

of $D_3$. End-functionalization or coupling with trimethylchlorosilane or dimethyldichlorosilane, respectively, proceeded satisfactorily (Scheme 1, eq 6). Thus, number-average MW's of AB1 and AB2 approximately doubled, giving ABA1 and ABA2, respectively (Table 2), and no shoulders corresponding to the precursor were visible in the SEC of the PAMS-*b*-PDMS-*b*-PAMS copolymers. As shown in Table 2, the AB and ABA PAMS−PDMS block copolymers had masses ranging between 8.2K and 56K and polydispersities of between 1.09 and 1.20 (Figure 3). Number-average MW's determined by SEC using PS standards were in good agreement with that determined by SEC analysis of the precursors and NMR integration of the PDMS−EDS and PAMS blocks.

The absence of the oligostyrene end block resulted in an increase of about 9 °C in the $T_g$ of the PAMS−EDS block compared to that of the PAMS−PS precursor blocks reported by Saam (Table 3). Higher MW PAMS blocks should have a much larger glass transition temperature as suggested by the values listed in Table 3. For instance, the $T_g$ of PAMS homopolymer with a MW comparable to that of PAMS−PS(3) is more than 20 °C higher. The effect on the glass transition temperature of the end-functionalization of PAMSLi with EDS is relatively small, amounting to only 2−3 °C (Table 3).

## Discussion

During the $D_3$ polymerizations listed in Tables 1 and 2, samples were taken directly for SEC and NMR analysis without termination.[31] As indicated above, this allowed detection of problems such as broadening of the MW distributions during polymerization and coupling of the copolymer anions as illustrated in Figure 4. The SEC chromatogram of the sample after addition of 10% $Me_2SiCl_2$ showed a high molecular weight peak corresponding to the ABA copolymers. Upon further addition of $Me_2SiCl_2$ the low molecular MW precursor peak decreases, indicating the formation of the ABA block copolymer. These coupling reactions were rapid (minutes) and quantitative as shown by the absence of a low MW shoulder if excess of $Me_2SiCl_2$ was avoided. This was done by slow addition of $Me_2SiCl_2$ and frequent SEC monitoring. At high $D_3$ conversions, requiring longer polymerization times, molecular weight distributions tended to broaden, especially when $D_3$ conversions were above 80% (Table 1, AB12, AB33). However, for shorter polymerization times and corresponding lower $D_3$ conversions the MWD's of the PDMS block tend to be narrower (Table 2, AB2, ABA2).

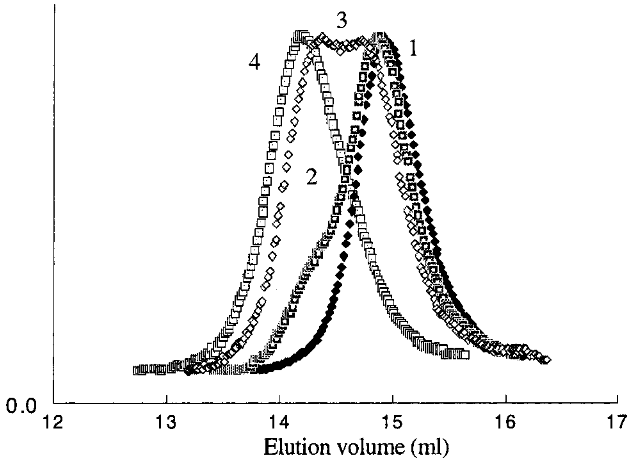


**Figure 4.** SEC chromatograms of Table 2. PAMS−EDS-*b*-PDMS AB2 (curve 1), after addition of 10% $Me_2SiCl_2$, (curve 2) after addition of 55% $Me_2SiCl_2$ (curve 3) and coupled PAMS−EDS-*b*-PDMS−EDS−PAMS ABA2 (curve 4).

As pointed out above, this is consistent with either PDMS redistribution reactions or the occurrence of lithium silanolate aggregation. Thus, the silanolate anion may attack the silicon of PDMS by intermolecular or intramolecular redistribution reactions (Scheme 2). Intermolecular PAMS−PDMS anion redistribution reactions are predicted to give lengthened or shortened PAMS−PDMS anions leading to a MW broadening (path a) or terminated PAMS−PDMS−PAMS and PDMS dianions (path b). The intramolecular redistribution reactions are expected to lead to terminated cyclic PDMS and shortened PAMS−PDMS chains (a), but in this case pathway b has no effect. Following this mechanism the broadening of MWD's may be minimized by shorter reaction times made possible by higher concentrations of $D_3$ coupled with the use of shorter reaction times (lower conversions).

As postulated by Maschke et al., the MW broadening of PDMS at higher conversions may also be due to lithium silanolate aggregates, the fraction of which decreases with increased monomer conversion.[12] Thus, as the polymer chains grow longer, the fraction of aggregated ion pairs decreases due to increased excluded-volume effects. As a result, the polymerization rates increase and MW distributions widen. These problems should be more serious in hydrocarbons with polar additives than in the present case since in the more polar THF the degree of aggregation should be less pronounced. Furthermore, the interconversion between aggregated and nonaggregated lithium silanolates is expected to be faster on the polymerization time scale. Thus, inter- and/or intramolecular redistribution reactions mediated by lithium silanolates seem a more plausible cause for the narrowed distributions at lower $D_3$ conversions.

## Conclusions

The use of 2−3 equiv of 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane as end-capping agent at −10 °C in THF following the *t*-BuLi initiated anionic polymerization of AMS in THF at −78 °C quantitatively gives stable and colorless PAMS−EDSLi silanolates that may be used as initiators for the polymerization of hexamethylcyclotrisiloxane. Termination of the silanolate end groups with $Me_3SiCl$ and coupling with $Me_2SiCl_2$ allows the synthesis of narrow distribution PAMS−PDMS and PAMS−PDMS−PAMS block copolymers without the use of styrene as an end-capping block. The glass transition temperatures of the PAMS end blocks are appreciably higher than the corresponding PAMS−PS blocks.

**Acknowledgment.** We thank Ray Yin for his help with DSC measurements. Support for this work was provided by NSF-DMR Polymer Program (DMR 9101558) and by MURI/AFOSR 49620-96-1-0035.

## References and Notes

(1) Saam, J. US Patents 3,483,270, 1972; 4,107,227, 1978.
(2) Morton, M. US Patent 3,051,684, 1962.
(3) Kendrick, T. C. US Patent 3,890,405, 1975.
(4) Curran, S.; Kim. J.; Han, C. D. *Macromolecules* **1992**, *25*, 4200.
(5) Cowie, J. M. G.; Toporowski, P. M. *J. Macromol. Sci., Phys.* **1969**, *B3*, 81.
(6) Widmaier, J. M.; Mignard, G. *Eur. Polym. J.* **1987**, *23*, 989.
(7) Worsfold, D. J.; Bywater, S. *J. Polym. Sci.* **1957**, *26*, 299.
(8) Zhuang, J.; Andrews, A. P.; Greer, S. C. *J. Chem. Phys.* **1997**, *107*, 4705.
(9) Kim, J. K.; Han, C. D. *Macromolecules* **1992**, *25*, 27.
(10) For anionic polymerization of AMS, see: (a) Bui, V. T.; Leonard, J. *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 1745. (b) Krause, S.; Dunn, D. J.; Seyed-Mozzaffari, A.; Biswas, A. M. *Macromolecules* **1977**, *10*, 786. (c) Baer, M. *J. Polym. Sci., Part A* **1964**, *2*, 417. (d) Hensen, D. R.; Shen, M. *Macromolecules* **1975**, *8*, 903.
(11) Elias, V. H. G.; Kamat, V. S. *Makromol. Chem.* **1968**, *117*, 61.
(12) Maschke, U.; Wagner, T. *Makromol. Chem.* **1992**, *193*, 2453.
(13) Suzuki, T.; Okawa, T. *Polym. Commun.* **1988**, *29*, 225.
(14) Suzuki, T. *Polymer* **1989**, *30*, 333.
(15) Zilliox, J. G.; Roovers, J. E. L.; Bywater, S. *Macromolecules* **1975**, *8*, 573.
(16) Kawakami, Y.; Miki, Y.; Tsuda, T.; Murthy, R. A. N.; Yamashita, Y. *Polym. J.* **1982**, *14*, 913.
(17) Lestel, L.; Boileau, S. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 293.
(18) Lee, C. L.; Johannson, O. K. *J. Polym. Sci (Chem. Ed.)* **1976**, *14*, 729.
(19) Yin, R.; Hogen-Esch, T. E. *Macromolecules* **1993**, *26*, 6952.
(20) Yin, R.; Amis, E. J.; Hogen-Esch, T. E. *Macromol. Symp.* **1994**, *85*, 217.
(21) Berger, P. A.; Kotyk, J. J.; Remsen, E. *Macromolecules* **1992**, *25*, 7227.
(22) Bryce, W. A. J.; Meldrum, I. G.; McGibbon, G. *Polymer* **1970**, *11*, 394.
(23) Spach, G.; Levy, M.; Szwarc, M. *J. Chem. Soc.* **1962**, 355.
(24) Wang, L. S.; Phalip, P.; Favier, J. C.; Sigwalt, P. *J. Appl. Polym. Sci.* **1994**, *54*, 1439.
(25) Ades, D.; Fontanille, M.; Leonard, J. *Can. J. Chem.* **1982**, *60*, 564.
(26) Suzuki, T. *Polymer* **1989**, *30*, 333.
(27) The anionic polymerization of EDS has been reported: Chonowski, J.; Mazurek, M. *Makromol. Chem.* **1975**, *176*, 2999.
(28) Dainton, F. S.; Hui, K. M.; Ivin, K. J. *Eur. Polym. J.* **1969**, *5*, 387.
(29) Wyman, D. P.; Song, I. H. *Die Makromol.* **1968**, *115*, 64.
(30) Yu, Y. S.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 1753.
(31) Hogen-Esch, T. E.; Mason, J. R; Ladd, B. J.; Helary, G.; Belorgey, G. In *Contemporary Topics in Polymer Science, Advances in New Materials*; Riffle, J., Salamone, J. C., Eds.; Plenum Press: New York, 1992; Vol. 7, p 339.

MA001452Z