Living Anionic Polymerization of Hexamethylcyclotrisiloxane (D_3) Using Functionalized Initiation

Casey L. Elkins and Timothy E. Long*

Department of Chemistry, Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

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Introduction

Poly(dimethylsiloxane) (PDMS) possesses a variety of properties that are attractive for many industrial applications.[1] PDMS exhibits excellent thermal and oxidative stability as well as low absorption in the UV and good oxygen reactive ion etch resistance. This latter attribute is important in microelectronics applications.[2] PDMS also has high chain flexibility, low glass transition temperature, low surface energy, and a low solubility parameter.[1] Telechelic PDMS is readily synthesized via the catalyzed ring-opening polymerization of octamethylcyclotetrasiloxane (D_4).[3] However, this equilibration process yields both linear polymers and cyclic oligomers, and a broad molecular weight distribution is observed. In 1969, Frye et al. proposed the use of the cyclic trimer hexamethylcyclotrisiloxane (D_3) in the synthesis of narrow molecular weight distribution PDMS.[4,5] Because of the increased ring strain in the D_3 monomer, the rate of polymerization is greater and living anionic polymerization occurs faster than D_4 ring−chain equilibrium reactions. Thus, well-defined polymers with narrow molecular weight distributions are attainable. In general, the polymerization of D_3 is initiated using an alkyllithium reagent in a nonpolar solvent such as cyclohexane at room temperature. These reaction conditions result in the formation of a monoadduct of initiator with D_3, and DeSimone et al. recently confirmed the formation of this monoadduct using time-of-flight matrix-assisted laser desorption ionization mass spectrometry (TOF-MALDI-MS).[6] The reaction will not proceed further without the addition of a polar promoter to the nonpolar hydrocarbon solvent.[5] Upon addition of a promoter, the polymerization proceeds until all monomer is consumed and the living siloxanolate is terminated. Typical promoters for these polymerizations include tetrahydrofuran (THF),[7,8] diglyme,[9] triglyme,[8] and dimethyl sulfoxide (DMSO).[7] These promoters are complexing agents for lithium cations, and it was reported earlier that the amount of original silanolate aggregates was reduced, leading to an increased propagation rate and the avoidance of side reactions.[10] However, it was determined that at conversions greater than 85% D_3 polymerizations also suffer from backbiting reactions.[11] Backbiting reactions consist of intramolecular attack of the living siloxanolate chain end and the subsequent formation of deactivated unstrained rings.[12] At high monomer concentrations, the molecular weight increased in a linear fashion with monomer conversion; however, as the reactions approached high conversion, monomer starved conditions facilitated backbiting reactions. Several methods were used to minimize or eliminate these deleterious side reactions. The simplest approach was intentional termination prior to side reactions, typically at 80−85% conversion.[8,13] This was an effective method to avoid these side reactions from occurring; however, this approach resulted in lower yields.

Living anionic polymerization provides many benefits over conventional free radical polymerization. Living anionic polymerization permits the synthesis of polymers with controlled molecular weight and a narrow molecular weight distribution. Stereochemical control, synthesis of block and graft copolymers, and functionalization reactions at the polymer chain ends are also possible. In general, polymers that are prepared using organolithium initiators are end-functionalized with a variety of postpolymerization reactions involving electrophilic agents.[14,15] However, many functionalization reactions are not quantitative and result in a mixture of chain end functionality.[14] An alternative for the synthesis of end-functionalized polymers is the use of functionalized alkyllithium initiators, and functionalized alkyllithium initiators ensure quantitative chain end functionalization. It is generally necessary to use a protecting group in the initiator because most functionalities of interest, such as hydroxyl, carboxyl, or amino, are not stable in the presence of organolithium reagents.[16−18] A suitable protecting group is stable during anionic polymerization but also readily removed after polymerization to generate the desired functional group.[19]

The use of functionalized initiators offers several advantages over conventional electrophilic termination reagents for the synthesis of end-functionalized polymers.[20] Each functionalized initiator molecule will produce a macromolecule with the desired functionality at the chain end regardless of the molar mass of the polymer. The use of functionalized initiators also avoids the problems associated with electrophilic addition reagents, such as efficient and rapid mixing with viscous polymers, the stability of the anionic chain end, and selective reactivity.[14] Functionalized initiators also facilitate the synthesis of telechelic and heterotelechelic polymers, functionalized block polymers, and star-branched polymers with functional groups at each arm terminus.[19]

Experimental Section

Materials. Hexamethylcyclotrisiloxane (D_3) was stirred over calcium hydride at 80 °C for 48 h, allowed to cool, degassed several times, and vacuum-distilled (0.10 mmHg, 23−25 °C). 3-[(*N*-Benzyl-*N*-methyl)amino]-1-propyllithium (FMC Corp. Lithium Division, 0.95 M in cyclohexane), Pd/C (10 wt % Pd on activated carbon, Aldrich), and hydrogen (99.99%, Holox) were used without any further purification. Trimethylchlorosilane (Aldrich) was vacuum-distilled from calcium hydride. Cyclohexane was stirred over sulfuric acid for 7 days, decanted, and distilled under nitrogen from sodium immediately prior to use. Tetrahydrofuran (THF) was distilled under nitrogen from sodium and benzophenone immediately prior to use.

Polymer Synthesis. A 100 mL round-bottomed flask containing anhydrous cyclohexane (18.5 mL, 0.185 mol) and D_3 (10 g, 0.045 mol) was heated to 30 °C. 3-[(*N*-Benzyl-*N*-methyl)amino]-1-propyllithium (1.05 mL, 1 mmol) was added to the solution to initiate the polymerization. The reaction was allowed to proceed for 4 h. After 4 h, THF (2 mL, 0.25 mol) was added to the reaction. The reaction was allowed to proceed for an additional 45 h. The reaction was terminated via the addition of trimethylchlorosilane (0.19 mL, 1.5 mmol).

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Scheme 1. Anionic Polymerization of D_3 Using 3-[(*N*-Benzyl-*N*-methyl)amino]-1-propyllithium

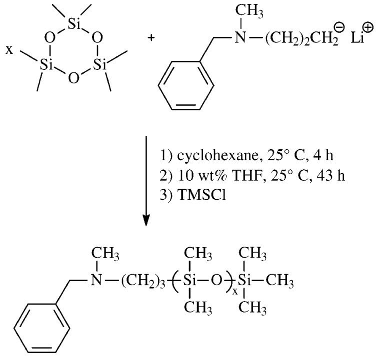


Table 1. Characterization of the Poly(dimethylsiloxane) Homopolymers Prepared via Anionic Polymerization

sample	M_n(calcd)	M_n[a]	M_n[b]	M_w/M_n[a]
PDMS-1	2400	2320	2380	1.13
PDMS-2	3750	2700	3260	1.13
PDMS-3	7500	5740	5400	1.13
PDMS-4	15000	17000	16500	1.03

[a] SEC conditions: THF, 40 °C, DRI detector. [b] Determined via ^{1}H NMR spectroscopy using the end group resonances assigned to the benzene ring in the initiator fragment between 7.1 and 7.4 ppm in comparison to the methyl groups on the silicon of the repeating unit found at 0 ppm.

Deprotection of Amine Functionality. A pressure vessel containing PDMS (5 g, 1.67 × 10^{-3} mol), THF (40 mL, 0.62 mol), and Pd/C (0.3 g) was pressured to 150 psi H_2 and placed in an oil bath at 100 °C. The reaction was allowed to proceed for 18 h. The reaction mixture was allowed to cool to room temperature and then filtered through a Celite bed to remove the catalyst. The solution was then concentrated and dried under vacuum.

Characterization. ^{1}H NMR spectra were determined in CD_2Cl_2 at 400 MHz with a Varian Unity spectrometer. Glass transition and melting temperatures were determined using a Perkin-Elmer Pyris 1 cryogenic DSC at a heating rate of 20 °C/min under nitrogen. Glass transition temperatures are reported as the inflection point of the change in heat capacity during the second heat. Molecular weights were determined using size exclusion chromatography (SEC) using a Waters 717plus equipped with a Waters 2410 refractive index detector, and a Wyatt Technology Minidawn MALLS detector was utilized for absolute molecular weight measurements. The d*n*/d*c* values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. SEC measurements were performed at 40 °C in tetrahydrofuran at a flow rate of 1.0 mL/min. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement.

Results and Discussion

A series of poly(dimethylsiloxane) (PDMS) homopolymers were synthesized using 3-[(*N*-benzyl-*N*-methyl)-amino]-1-propyllithium as shown in Scheme 1. Upon the addition of the pink/red 3-[(*N*-benzyl-*N*-methyl)amino]-1-propyllithium to the reaction mixture, a pink/red color was immediately observed. Over the initial 4 h reaction period, prior to the addition of the promoter, this color gradually faded to a yellow/orange color. It was postulated that this color shift was due to the formation of the monoadduct of initiator to D_3 monomer unit. Upon the addition of the promoter, THF, no further change in color was observed. Trimethylchlorosilane addition resulted in the immediate formation of lithium chloride salt and a colorless solution. The molecular weights and molecular weight distribution for a series of polymers are summarized in Table 1. As described previously, D_3 polymerizations suffer from backbiting reactions, which are typical for many ring-opening polymerization processes, if monomer starved conditions occur, i.e., conversion is greater than 85%. To avoid appreciable backbiting, our conversions were limited to 75%, and this was taken into consideration in the calculated molecular weights stated in Table 1. Yields were quantitative after considering the intentionally limited conversion (75%). The molecular weights obtained from SEC agreed well with those calculated on the basis of the grams of monomer to moles of initiator ratio. A factor that may contribute to discrepancies between calculated and SEC molecular weights is the reliance of the SEC refractive index detector on polystyrene standards. It is well-known that it is not possible to obtain absolute molecular weights for PDMS via multiple angle laser light scattering due to the fact that PDMS is isorefractive with THF, which is the SEC solvent used. Thus, the SEC molecular weights for the PDMS homopolymers are in comparison to polystyrene standards. These polymers also exhibited monomodal SEC traces as illustrated in Figure 1. The thermal transitions observed for the functionalized PDMS samples agreed with those typically found in the literature, with a T_g of −126 °C and a T_m of −45 °C.[21]

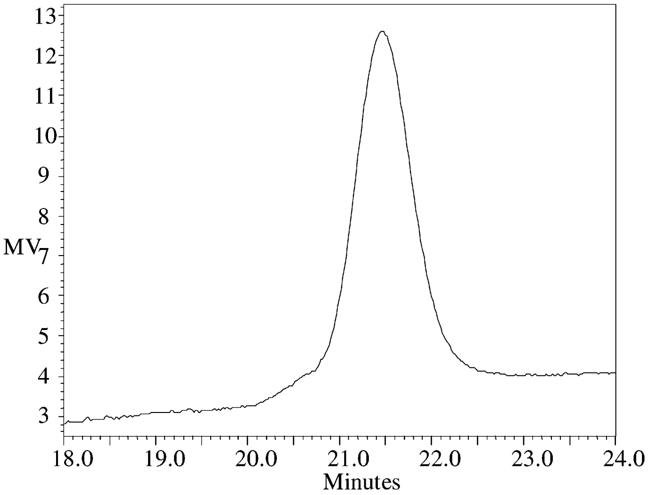
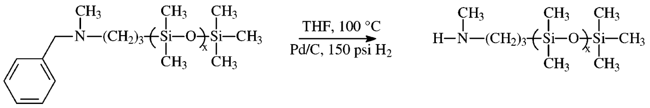


Figure 1. Monomodal SEC trace of 3.5K PDMS synthesized using 3-[(*N*-benzyl-*N*-methyl)amino]-1-propyllithium.

Scheme 2. Synthetic Methodology for the Deprotection of the Amine Functionality on PDMS



^{1}H NMR spectroscopic analysis was performed on the functionalized poly(dimethylsiloxanes). The number-average molecular weights were determined via comparing the end group resonances assigned to the benzene ring in the initiator fragment between 7.1 and 7.7 ppm to the methyl groups on the silicon of the repeating unit found at 0 ppm. ^{1}H NMR number-average molecular weights are particularly useful since PDMS is nearly isorefractive with THF, a typical SEC solvent. Thus, the PDMS peak in the SEC trace is relatively small, leading to a less accurate molecular weight determination.

The protecting group on PDMS was quantitatively removed by hydrogenolysis to yield a secondary amine,

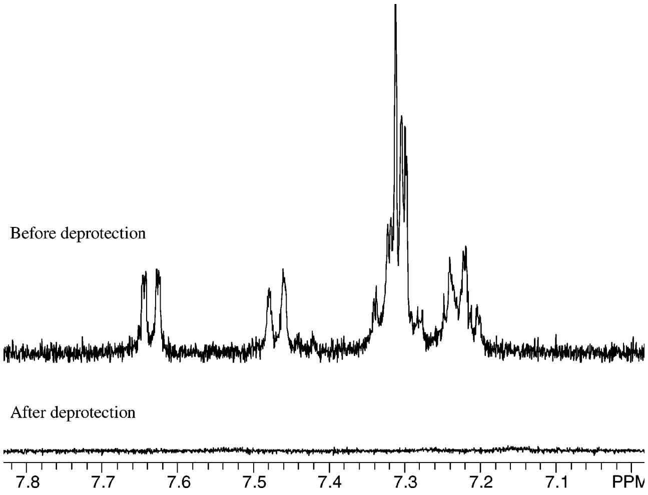


Figure 2. ^{1}H NMR spectra showing the quantitative removal of the benzyl protecting group to form a secondary amine terminal functionality. Polymer degradation was not observed.

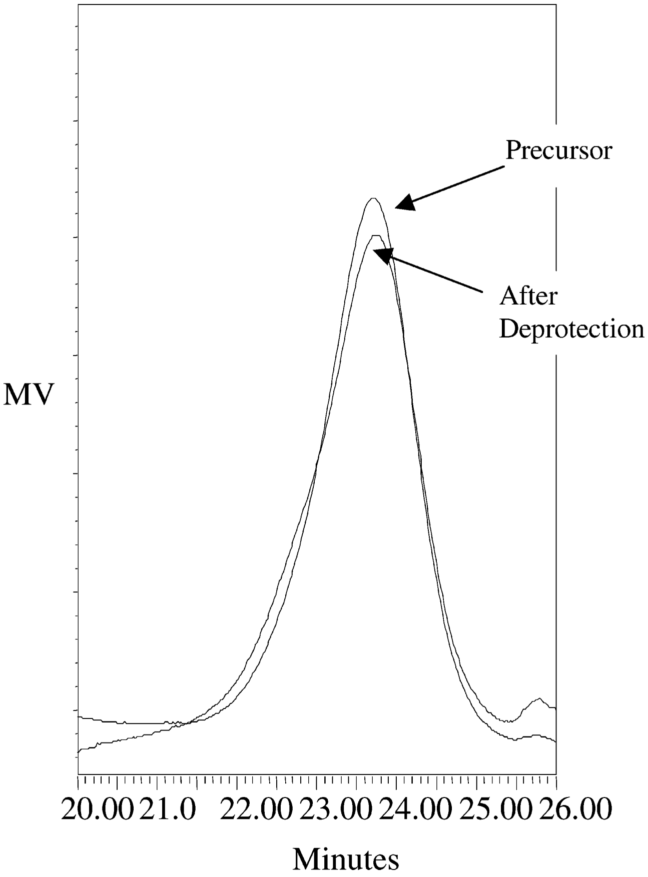


Figure 3. Overlap of monomodal SEC traces of amine functionalized 3.5K PDMS before and after deprotection.

as shown in Scheme 2. The polymer was dissolved in cyclohexane or THF in the presence of a catalyst, such as Pd/C. The temperature was raised to 100 °C with a hydrogen pressure of 150 psi. The removal of the protecting group was confirmed using ^{1}H NMR spectroscopy, and the reaction was quantitative for protecting group removal. The quantitative removal of the protecting group was observed in the ^{1}H NMR spectrum as shown in Figure 2. The upper ^{1}H NMR spectrum shows tertiary amine end-functionalized PDMS. After deprotection, the absence of resonances between 7.1 and 7.7 ppm indicated complete removal of the protecting group, as depicted in the lower ^{1}H NMR spectrum in Figure 2. The molecular weight and molecular weight distribution was unaffected by hydrogenolysis of the amine end group, as can be seen in the SEC trace shown in Figure 3. The secondary amine on the polymer chain end is amenable to many further functionalization reactions, which will be described in a future publication.

Conclusions

A series of PDMS homopolymers were synthesized via living anionic polymerization using a protected amine functionalized initiator. Controlled molecular weights and narrow molecular weight distributions were obtained. The protecting group was removed quantitatively to yield a secondary amine functionality at the polymer chain end. This secondary amine functionalized PDMS is suitable for diverse functionalization strategies.

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