Notes

Synthesis of Narrowly Dispersed Bis-Hydride-Capped Polydimethylsiloxane Using Difunctional Anionic Initiator Based on 1,3-Diisopropenylbenzene[†]

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Introduction

Linear siloxane polymers form an important class of inorganic polymers due to their widespread technological applications.[1−3] Poly(dimethylsiloxane)s, in particular, have been widely used as liquid silicone rubber, silicone oil, biomedical devices, polymer support for catalyst, insulating material for electronic applications, and comonomers for various thermoplastics by leveraging their highly flexible structure, high thermal stability, and an exceptionally low glass transition temperature.[4]

In general, linear siloxane polymers are prepared via two routes: acid-[4,5] and base-catalyzed[6] equilibrium ring-opening polymerization of cyclic organosiloxane and condensation of difunctional organosilanes and/or oligosiloxanes.[4b,7] Though the former technique is quite efficient in making polysiloxanes and is widely used, it leads to the formation of considerable amounts of cyclic organosiloxanes, resulting in the low yield of polymer and contamination of the product with low molecular weight cyclic oligomers. On the other hand, the condensation reactions involve coupling of organosilanols with hydrosilanes, which require expensive transition metal complexes as the catalyst with hydrogen gas as a byproduct. Apart from this, both these methods suffer from the drawback of broad molecular weight distribution along with the lack of control on molecular structure of the polymer.

Kinetically controlled anionic polymerization of cyclic trisiloxanes is well-known in yielding polysiloxanes with good yield, controlled molecular weight, and narrow polydispersity.[8,9] This is possible because anionic ring opening is generally faster than equilibration or redistribution reactions. Also, the propagating species (e.g., lithium silanolate) in anionic polymerization have weaker nucleophilicity than sodium, potassium, or cesium silanolate, etc., used in the equilibration reaction, which helps in the opening of cyclic siloxane to linear polymer without involving any equilibration and redistribution reactions of linear siloxane polymers.

Polymer chemists have resorted to anionic polymerization for preparing polysiloxane-based block copolymers with a wide range of unsaturated monomers, so as to utilize the unusual flexibility of polydimethylsiloxane chain and the inorganic character of its skeleton.[10] However, this strategy fails for polymers synthesized via condensation reaction as in that case monomers with reactive end groups at both ends are a prerequisite. Nonetheless, living anionic polymerization technique can be used to synthesize end-functionalized polymers containing a reactive end group at one or both chain ends in a simple and controlled manner.[11] To date, literature cites various examples for synthesis of narrowly dispersed polydimethylsiloxanes with only one end functional group via anionic polymerization; however, monodisperse polysiloxanes with functional groups at both ends are almost rare to find.[12] This paper reports the method for the preparation of narrowly dispersed difunctional terminated polydimethylsiloxane. The bis-hydride-capped polydimethylsiloxane was synthesized using a difunctional anionic initiator, which is generated in situ by reacting 1,3-diisopropenylbenzene (DIB) with *tert*-butyllithium (*t*-BuLi). The polysiloxane with functional groups at both ends was well characterized by FTIR spectroscopy, NMR (^{1}H and ^{29}Si) spectroscopy, gas chromatography (GC), and gel permeation chromatography (GPC).

Experimental Section

Materials and Methods. 1,3-DIB, *t*-BuLi (1.6 M), hexamethylcyclotrisiloxane (D_3), chlorodimethylsilane, and anhydrous tetrahydrofuran (THF) were purchased from Aldrich and were used without any further treatment. All reactions were run under a nitrogen atmosphere.

^{1}H and ^{29}Si NMR spectra were obtained on Bruker AMX-400 MHz spectrometer. Spectra of hydride-terminated polydimethylsiloxanes were run in deutrated chloroform ($CDCl_3$) at 25 °C. Infrared spectra were routinely obtained as neat fluid on a Perkin-Elmer FT infrared spectrometer. The molecular weight distribution of the bis-hydride-terminated polydimethylsiloxanes was analyzed using GPC at 25 °C on a Shimadzu (A-10 series) system equipped with a refractive index detector. THF was used as an eluent at the flow rate of 1 mL/min. The retention time of polysiloxanes were calibrated against the polystyrene standards.

Polymerization Procedure. Anionic polymerization of D_3 was carried out in an inert atmosphere in a previously flamed glass reactor equipped with a rubber septum. In a typical experiment, 50 mL of anhydrous THF was taken in a three-neck round-bottom flask, followed by the addition of 1,3-DIB (0.625 g, 0.0093 mol) and *t*-BuLi (5.1 mL, 0.0087 mol) at −20 °C. The resulting red reaction mixture was stirred at room temperature for 2 h. The monomer D_3 (13.2 g, 0.0595 mol) was added to reaction mixture dropwise at −20 °C and stirred for 4 h. The hydride capping was achieved by quenching the lithium by adding dimethylchlorosilane (0.587 g, 0.00872 mol) dropwise in the presence of triethylamine (TEA) at 0 °C for 2 h. Hexane (40 mL) was added to precipitate all the salt, which was then filtered. This process was repeated three times to remove all the salt. The volatiles were removed in vacuum to get clear hydride-terminated polydimethylsiloxane fluid.

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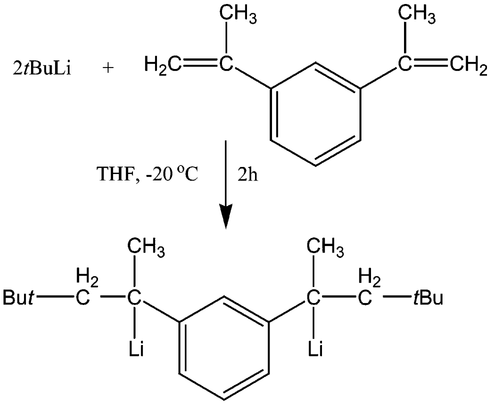
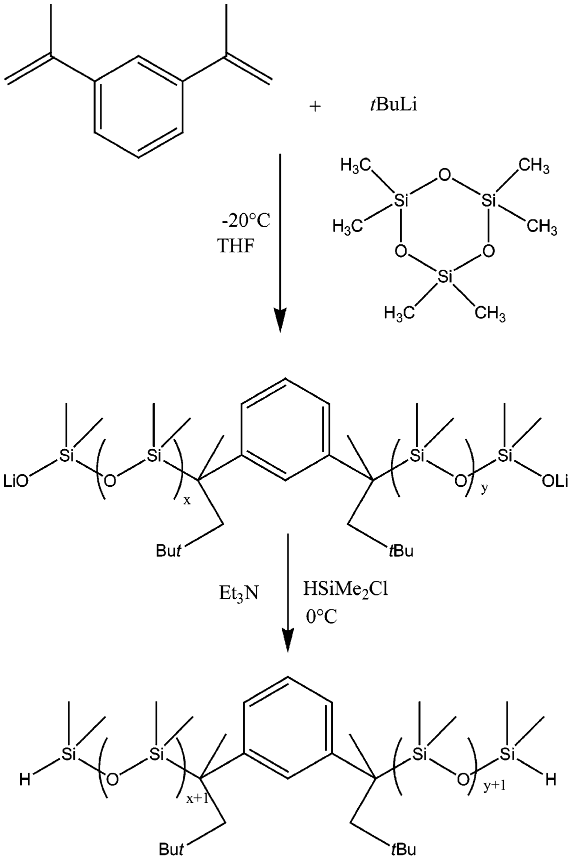
Scheme 1. Synthesis of Difunctional Initiator via the Addition Reaction of *t*-BuLi with 1,3-DIB



Scheme 2. Preparation of Narrowly Dispersed Bis-Hydride-Terminated Polydimethylsiloxane (1) via Anionic Polymerization



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Results and Discussion

The cyclotrisiloxanes have higher ring-opening tendency as compared to octamethylcyclotetrasiloxane (D_4) due to the increased ring strain. As per the calorimetric calculations of the equilibration reactions, the ring strain energy of D_3 is about 2−4 kcal/mol as compared to almost strain less D_4 (0.25 kcal/mol).[13] Thus, the bis-hydride-terminated poly(dimethylsiloxane) was prepared by the nonequilibrium anionic polymerization of D_3. The most commonly used initiating reagent for anionic polymerization of cyclic siloxane is *n*-BuLi, which results in monofunctional terminated polysiloxane.[8,9] However, an efficient difunctional anionic initiator is needed to synthesize the polysiloxane with reactive groups at both ends. Recently, 1,3-DIB emerged as an useful precursor for the synthesis of difunctional anionic initiator,[14] which can be a potential candidate for synthesizing polydimethylsiloxane having very narrow molecular weight distribution along with hydride functionalities at both ends.

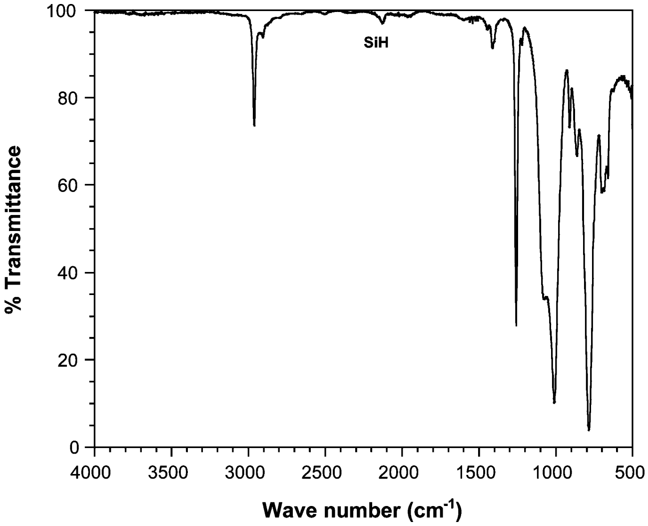

Figure 1. IR spectrum of **1** (neat) at 25 °C; ν_{Si-H} at 2129 cm^{-1} indicates the presence of the Si−H end functionality.

Two common methods have been explored to make difunctional initiators, viz. the coupling of radical anions[15] and the reaction of monofunctional organolithium compound with a molecule containing two double bonds of high ceiling temperature in order to avoid the competition between metalation and homopolymerization.[14] More recent efforts have been focused on the latter method, and 1,3-DIB is preferred over the other precursors containing two nonconjugated double bonds due its low cost and commercial availability. There have been efforts to synthesize pure lithium diadduct using butyllithium and 1,3-DIB which results in addition reaction along with polymerization of metalated 1,3-DIB. It was realized that a pure diadduct was obtained only by the reaction of 1,3-DIB with *t*-BuLi as there was formation of undesired oligomers in the case of *n*-BuLi or *s*-BuLi. The relative temperature effect on the addition and polymerization steps can be assessed from the activation energy of these two processes. In general, the rate of polymerization decreases more significantly as compared to the rate of addition on lowering the temperature. However, it was observed that the rate of addition of 1,3-DIB and *s*-BuLi was affected by the polarity of solvent and was found to be significantly low in nonpolar solvents at low temperature. Moreover, in nonpolar solvents, the bianionic chains having Li at both the ends form very large network-like aggregates.[16] Hence, usage of polar additive/solvent is quite crucial in enhancing the rate of addition reaction.

The dilithium initiator was prepared by the stoichiometric reaction of *t*-BuLi with 1,3-DIB in THF at low temperature (Scheme 1). The progress of reaction was monitored by the ^1H NMR spectrum. The signals at δ 5.16 and 5.46 due to unsaturated olefin groups in 1,3-DIB disappeared after 1 h of reaction time, suggesting the completion of reaction between 1,3-DIB and *t*-BuLi. This inference is further fortified by the absence of peak due to 1,3-DIB in gas chromatography. Then, monomer (D_3) was added dropwise to red *t*-BuLi/1,3-DIB adduct at −20 °C and stirred for 3 h (Scheme 2). The completion of polymerization was followed by end-capping with chlorodimethylsilane as chlorosilanes have a higher reactivity for termination reactions as compared to alkyl halide derivatives

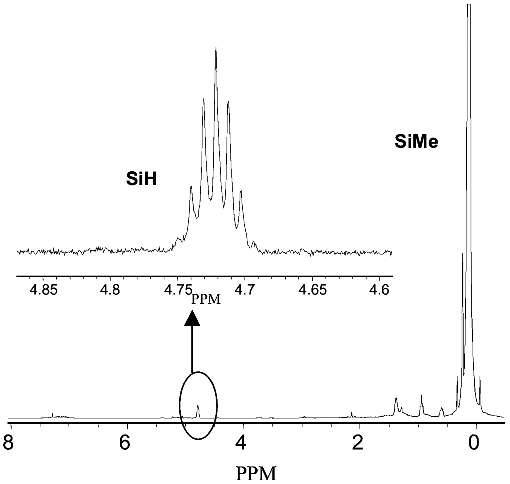

Figure 2. ^{1}H NMR spectrum of **1** in $CDCl_3$ at 25 °C. The absence of unsaturated olefinic protons of 1,3-DIB and the appearance of Si−H end groups in the spectrum should be noted, as this indicates the completion of addition and coupling reaction, respectively.

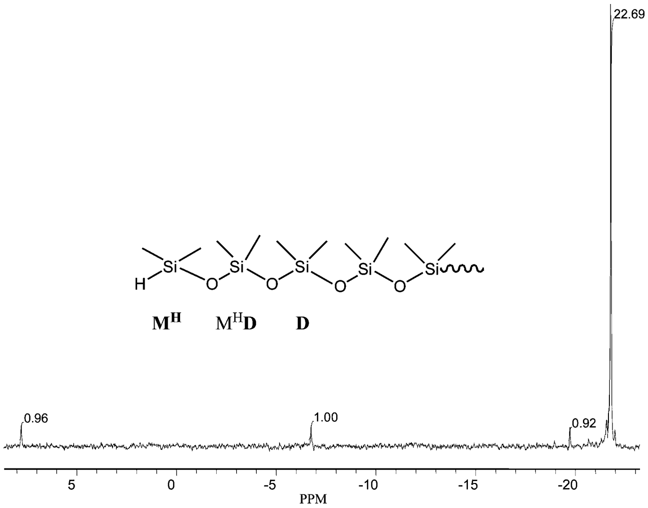

Figure 3. ^{29}Si NMR spectrum of **1** in $CDCl_3$ at 25 °C. The integration ratio (1:1) of terminal Si−H group (δ −6.8) and silicon atom connected to 1,3-DIB (δ 7.6) in the spectrum confirms the structure of **1**.

due to their highly polarized silicon−chlorine bond. This provides a highly efficient methodology for the quantitative introduction of a wide range of functional groups.[17]

The hydride-terminated polysiloxane (**1**) was well characterized by IR, ^{1}H NMR, ^{29}Si NMR spectroscopy, and GPC. The IR spectrum of **1** showed a weak absorption band due to Si−H stretching at 2129 cm^{-1} and Si−H bending vibrations at 912 cm^{-1} (Figure 1).[18] In addition, the spectrum also revealed other characteristic bands of **1** due to Si−O−Si and Si−Me groups ($\nu_{Si-O-Si}$ at 1010 cm^{-1} and ν_{Si-Me} at 1257 cm^{-1}).

The presence of Si−H end group was further supported by the ^{1}H NMR spectrum of **1**. Figure 2 shows a ^{1}H NMR spectrum that revealed distinct signal at δ 4.72 due to Si−H end groups. The chemical shift value of Si−H protons is consistent with earlier reports.[18] The spectrum also showed well-resolved heptads in the SiH region with $^{3}J_{SiH}$ of 3.1 Hz. The spectrum also detects aromatic protons at δ 7.09−7.41 and protons due to butyl groups of 1,3-DIB around δ 0.70−2.18. The integration ratio of Si−H and Si−Me groups indicates that Si−H groups are present at the both ends of polydimethylsiloxane. The ^{1}H NMR spectrum was also used for calculating degree of polymerization. The "*d*" length [$-OSi(Me_2)O-$ unit] of **1** was found to be ∼46, which was in agreement with theoretical "*d*" length, calculated based on molar ratio of monomer and initiator for the synthesis of **1**.

The presence of Si−H end groups and "*d*" length was further confirmed by the ^{29}Si NMR spectrum (Figure 3). The spectrum showed signals at δ 7.6, −6.8, −19.8, and −21.9 for Si−C (silicon atom connected to DIB), Si−H, $M^{H}D$ units, and D units, respectively. The ^{29}Si NMR spectrum further authenticates the assignments done on the basis of the ^{1}H NMR spectrum. The integration ratio of Si−H and Si−Me groups clearly demonstrates the presence of hydride at both ends of polysiloxane. The "*d*" length was calculated to be 47.4, which is similar to that attained by the ^{1}H NMR spectrum.

GPC data of **1** revealed the weight-average molecular weight (M_w) and polydispersity (PDI) to be 5156 and 1.12, respectively. The difunctional terminated polysiloxane (**1**) synthesized via this method has significantly less PDI (1.12) as compared to prepared by cationic ring-opening polymerization (PDI ∼ 2.5−3.0). The *t*-BuLi/1,3-DIB adduct for the ring-opening polymerization of D_3 leads to efficient propagation and monomodal distribution of the molecular weight.

Conclusions

We have demonstrated in this paper how monodisperse polydimethylsiloxane with hydride at both the ends can be prepared by anionic ring-opening polymerization of D_3 using *t*-BuLi/1,3-DIB as an initiator. Multinuclear NMR spectra and GPC data confirm the formation of narrowly disperse bis-hydride-terminated polysiloxane fluid, synthesized via this route. This knowledge can be potentially utilized for the development of a wide range of functionalities at both chain ends in polydimethylsiloxane by using the well-established chemical reactivity of Si−H end groups via hydrosilylation reaction, thereby broadening their scope as comonomers for manufacture of organic/inorganic hybrid copolymers via condensation polymerization.

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