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RAPID PURIFICATION AND CHARACTERIZATION OF POLY(HYDROGENMETHYLSILOXANE)

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NOTE

RAPID PURIFICATION AND CHARACTERIZATION OF POLY(HYDROGENMETHYLSILOXANE)

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ABSTRACT

This paper details an efficient method to obtain Poly(hydrogenmethylsiloxane) (PHMS) free from low molecular weight impurities. High temperature, high vacuum distillation was used to remove the volatile components of commercially available PHMS to afford high molecular weight products with a PDI significantly lower than the commercial material. The native and distilled polymers were compared by characterization techniques including gas chromatography (GC), proton nuclear magnetic resonance spectroscopy (^{1}H-NMR), and gel permeation chromatography (GPC).

Key Words: Poly(hydrogenmethylsiloxane) (PHMS); Gas chromatography; Vacuum distillation; Purification

INTRODUCTION

PHMS is an important polymer in several applications due to its reactive silane bond. This silane bond can be utilized to give silicone rubbers [1] via a hydrosilation reaction between the Si-H bond and an olefin crosslinking agent. The Si-H bond can also be utilized as a chemoselective reducing agent.[2] Side chain liquid crystalline polymers [3] and liquid crystalline elas-

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tomers [4] have been reported utilizing PHMS as backbone polymer, with mesogenic groups attached by a hydrosilation reaction.

Commercial PHMS is generated by hydrolysis of methyldichlorosilane. This process leads to a polymer of broad polydispersity, containing oligomeric and low molecular weight cyclic byproducts, which are undesirable for many applications. In the case of a crosslinked elastomer, a significant amount of low molecular weight cyclics and oligomers can reduce the number of effective crosslinks within the elastomeric network. Therefore, PHMS requires purification in order to be used in this fashion, and a method of fractional precipitation has been reported by Hawthorne.[5] While this method is effective, it is time consuming, requiring one week to complete. Schatz has shown the vacuum distillation of poly(dimethylsiloxane) (PDMS) can be used to isolate individual oligomers with a discrete degree of polymerization (DP) with a range of $n = 2–10$ followed by gas chromatography (GC) to characterize the oligomers.[6] The investigation described below pursues the purification of PHMS by high temperature, high vacuum distillation, and characterization by GC, ^{1}H NMR, and GPC.

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EXPERIMENTAL

General Methods and Materials

Poly(hydrogenmethylsiloxane) DC 1107 was obtained from Dow Corning. Bis(trismethylsiloxy)methyl silane and methyltris(trimethylsiloxy)-silane were obtained from Gelest. All other materials were obtained from Aldrich. Toluene was dried over sodium prior to use. ^{1}H NMR spectra were obtained on a Unity Innova 500 MHz spectrometer. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standard. Chloroform (δ 7.26 for ^{1}H) was used as an internal standard for chloroform-d. Low-resolution, fast atom bombardment (FAB) mass spectra were obtained on a Micromass ZAB-SE spectrometer. Electron impact ionization (EI), chemical ionization with *i*-butane (CI), field ionization (FI), and field desorption (FD) mass spectra were obtained on a Micromass–VSE spectrometer. Low-resolution matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained using 2,5-dihydroxybenzoic acid (DHBA) as the matrix. Gas chromatography was performed using a Hewlett-Packard 5890 with a 50 m HP-1 capillary column and a flame ionization detector. The oven temperature was initially 80°C, followed by heating to 230°C at 10°C/min, then held for 20 minutes. Injections were 1 μL of a 100 mg/mL solution in CH_2Cl_2. Infrared spectroscopy was performed with a salt plate using a Nicolet Nexus 670 FT-IR spectrometer. Gel permeation chromatography (GPC) measurements were performed in tetrahydrofuran (THF) with a Waters 515 HPLC pump, a Viscotek model 300 triple detector

array, and a series of three Polymer Laboratories Plgel 10 μm mixed bed light scattering (7.8×300 mm) columns. Molecular weight data were obtained using Viscotek's TriSEC software. The light scattering constant, mass constant, and viscosity constant were determined from a single 90 kDa narrow polystyrene standard and checked against other known polystyrene standards for accuracy.

Distillation Technique

To a 100 mL round bottom flask equipped with a magnetic stir bar and distillation apparatus was added PHMS (50 mL). The flask was evacuated to 200 mTorr and then placed in a hot silicon oil bath (210°C). Over 3 hours, the distillate was collected in a single receiving flask. The solution was cooled to room temperature, flushed with N_2, and the distillate was discarded. The mother liquor was recovered, which contained the high molecular weight fraction (ca. 30 mL). ^{1}H NMR (500 MHz, $CDCl_3$, δ) 4.71 (Si-*H*, 71 H), 0.20 (Si-CH_3, 220 H), 0.12 (Si-(CH_3)$_3$, 18 H).

PHMS Modification with Styrene

To a dry 20 mL round bottom flask equipped with a magnetic stir bar and septum was added PHMS (0.19 g, 3.0 mmol, 1 equiv). The flask was evacuated and backfilled with N_2. Dry toluene (ca. 10 mL) was added via cannula. Styrene (2.08 g, 20 mmol, 6.7 equiv) was added via syringe, and the resulting solution was stirred for ca. 5 minutes. Dichloroplatinum-cyclooctadiene in CH_2Cl_2 (1% w/w, 100 μL) was added via syringe, and the resulting solution was stirred at room temperature for 16 hours. The reaction was monitored by IR spectroscopy for the disappearance of the Si-H stretch ($\upsilon = 2165$ cm^{-1}), and the reaction was complete after 20 hours. The solvent and excess styrene were removed in vacuo. The resulting material was characterized by THF GPC.

RESULTS AND DISCUSSION

Commercial PHMS (Dow DC 1107) was vacuum distilled for 3 hours under high vacuum conditions. The distillate (low molecular weight fraction) was discarded, and the mother liquor (high molecular weight fraction) was characterized and compared to commercial PHMS.

The commercial PHMS showed many signals prior to a retention time (T_R) of 10 minutes. The appearance and intensity of the early T_R peaks was greatly reduced for the distilled PHMS. While Schatz [6] has shown that a GC

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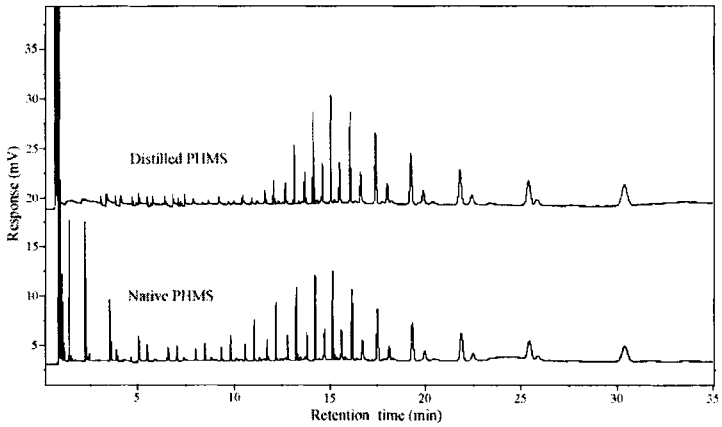

Figure 1. GC chromatograms of native and distilled PHMS.

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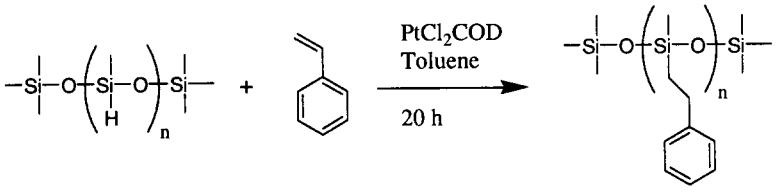
can provide repeat resolution up to $n = 10$ for PDMS samples, the GC chromatogram in Fig. 1 appears to show resolved peaks for each degree of polymerization up to $n = 40$. Peak assignment was attempted with GC/MS, but due to the instability of the ionized PHMS, no M^+ over 500 g/mol was found for the polymer, despite attempts with a variety of techniques including EI, CI,[7] FI, FD, FAB, or MALDI [8,9,10] ionization techniques. If each peak represents a discrete DP, then the distillation technique used in this work removes oligomers up to ca. $n = 18$ (1100 M_n).

GPC in THF was used to verify the apparent increase in M_n. The refractive index of PHMS is nearly identical to that of THF, so styrene was attached to the native and distilled polymers in quantitative yield (as measured by ^1H NMR spectroscopy) via a hydrosilation to provide better contrast.

The modified polymers were then characterized by GPC in THF. After adjusting the M_n for the weight of the styrene, the distilled PHMS showed a M_n of 5050 compared to 3500 for the native PHMS. More importantly, there was a significant decrease in the polydispersity index (PDI) of the distilled PHMS. After distillation, the PDI was reduced to 5.1, compared to 10.6 for the native polymer.



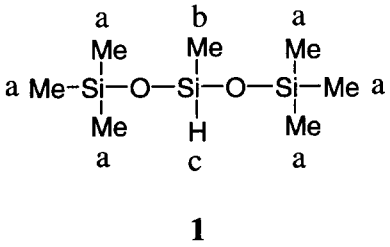
Scheme 1. Modification of PHMS by hydrosilation using styrene.

Table 1. Summary of Molecular Weight Data

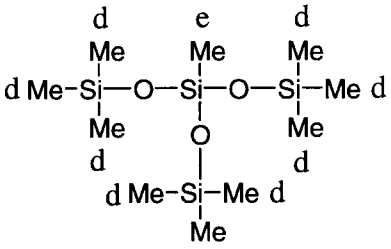
	GC DP Range	GPC in THF M_n	GPC in THF PDI	^{1}H NMR M_n
Native	1–40	3500	10.6	3960
Distilled	18–40	5050	5.1	4580

Although the GPC and GC results strongly indicated the removal of oligomeric material, there was the possibility of chain branching from the oxidation of a Si-H bond. Model compounds were studied to determine the characteristics of a branched unit and were compared to the distilled polymer.

Bis(trismethylsiloxy)methyl silane **1** was used as the linear analog, and methyltris(trimethylsiloxy)silane **2** was employed as the branched analog. Protons of the branched model compound methyl peak **e** were isolated from the rest of the silylmethyl peaks of both **1** and **2**. Examination of the region around 0 ppm would be able to determine the existence of branched polymers. As no signals in this region were observed for the purified PHMS spectra, there is no evidence that branch points are generated during the distillation.



1



2

Peak	δ (ppm)
a	0.11
b	0.10
c	4.62
d	0.09
e	-0.01

Figure 2. Structure and ^{1}H NMR chemical shifts of model compounds.

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Based upon the chemical shifts from the model compound study, end group analysis gave an $M_n = 3960$ for the native PHMS compared to $M_n = 4580$ for the distilled sample, in good agreement with the data obtained from GPC.

CONCLUSION

Presented is a method for the rapid and efficient removal of low-molecular weight material from commercial PHMS by vacuum distillation, followed by characterization with GC. This procedure may be used in place of other standard procedures, allowing the polymer to be purified and characterized within a matter of hours rather than days. Also, it has been shown that the distilled polymer can be characterized reliably by GC, GPC, or ^{1}H NMR.

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