



# Synthesis of 1,3-Bis(4-Hydroxybutyl)tetramethyldisiloxane and $\alpha,\omega$ -Bis(4-Hydroxybutyl)-polydimethylsiloxane

Li Yu and Chao-Can Zhang\*

School of Material Science and Engineering, Wuhan University of Technology  
Wuhan 430070, P.R. China

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## ABSTRACT

In this paper, using ethyl iodide and iodine as catalysts, 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane (BHBTMDS) was directly synthesized from dimethyldichlorosilane, purified tetrahydrofuran and magnesium powder.  $\alpha,\omega$ -Bis(4-hydroxybutyl) polydimethylsiloxanes (HB-PDMSs) with different number-average molecular weights could be prepared through the reaction of 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane and dimethoxydimethyl silane in the presence of a stoichiometric amount of water and hydrochloric acid. Structures of BHBTMDS and HB-PDMS were characterized by Fourier transform infrared (FTIR) spectroscopy and high-resolution  $^1\text{H}$  NMR. The number-average molecular weights of these hydroxybutyl-terminated polydimethylsiloxanes could be determined fairly by end group titration method. The results from FTIR and high-resolution  $^1\text{H}$  NMR clearly illustrated the successful syntheses of BHBTMDS and HB-PDMS. The number-average molecular weight of HB-PDMS obtained was higher than the targeted molecular weight. When the molecular weight is lower, the deviation between targeted number-average molecular weight and experimental number-average molecular weight was larger. At number-average molecular weight higher than 5,000 g/mol smaller deviation was observed.

## Key Words:

1,3-bis(4-hydroxybutyl)tetramethyldisiloxane;  
 $\alpha,\omega$ -bis(4-hydroxybutyl)-polydimethylsiloxane;  
synthesis;  
structure;  
end group titration.

## INTRODUCTION

Polydimethylsiloxanes (PDMSs) have many desirable features resulting from the presence of an inorganic siloxane backbone with organic methyl groups attached to the silicon, such as low surface energy, low-temperature flexibility based on a low glass-transition

temperature ( $\sim -123^\circ\text{C}$ ), high thermal stability [1], good release properties, and excellent dielectric insulating properties. Hydroxybutyl-terminated polydimethylsiloxane is one class of reactive organosiloxane polymers. The incorporation of low molecular weight polydi-

(\*) To whom correspondence to be addressed.

E-mail: [yuli75w@163.com](mailto:yuli75w@163.com)

methylsiloxane as a soft segment material to produce a polyurethane block polymer gave material with interesting bulk and surface properties due to the characters of the siloxane soft segment [2]. Because polydimethylsiloxane disilanols are prone to hydrolysis, more hydrolytically stable polydimethylsiloxane terminated with hydroxybutyl groups was used in this study.  $\alpha,\omega$ -Bis(4-hydroxybutyl) polydimethylsiloxane (HB-PDMS, 1) has only Si-C and C-OH bonds, and thus is more stable as compared to Si-OH and Si-O-C bonds of a silanol [3].

It was reported previously that 2,2-dimethyl-1-oxa-2-silacyclohexane [4] was synthesized using dimethyldichlorosilane, tetrahydrofuran, and magnesium powder as the starting materials, and using ethyl iodide and iodine as catalysts, but it was found that the reaction was very slow and much larger amounts of iodine were needed to catalyze the reaction. Then 2,2-dimethyl-1-oxa-2-silacyclohexane was readily converted by hydrolysis to 5,5,7,7-tetramethyl-6-oxa-5,7-disila-1,11-undecanediol [i.e. 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane (BHBTMDS, 2)] in the manner reported by Knoth et al. [5]. Lai et al. [6] reported that when hydroxybutyl-terminated PDMS was synthesized by 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane and dimethoxydimethyl silane in the presence of a stoichiometric amount of water and hydrochloric acid, the product gave the expected molecular weight. Because of limited commercial availability, only BHBTMDS can be used to prepare  $\alpha,\omega$ -bis(4-hydroxybutyl)polydimethylsiloxane. The price of BHBTMDS is very high and we can synthesize BHBTMDS with cheap materials. The major objective of this study was to obtain  $\alpha,\omega$ -bis(4-hydroxybutyl)polydimethylsiloxane that can form polyurethane-polydimethylsiloxane prepolymer that in turn can yield gradient polyurethane material with high thermal stability, good mechanical properties, interesting surface properties and so on. In the article, we study the synthesis of BHBTMDS with a simpler method. Using ethyl iodide and iodine as catalysts, 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane was directly synthesized from dimethyldichlorosilane, purified tetrahydrofuran and magnesium powder. Then BHBTMDS can be used to prepare HB-PDMSs by a method of polymerization that was described by Lai et al. [6]. Structures of BHBTMDS and HB-

PDMS were characterized by FTIR spectroscopy and high-resolution  $^1\text{H}$  NMR. The number-average molecular weights of these HB-PDMSs could be determined fairly by end group titration method.

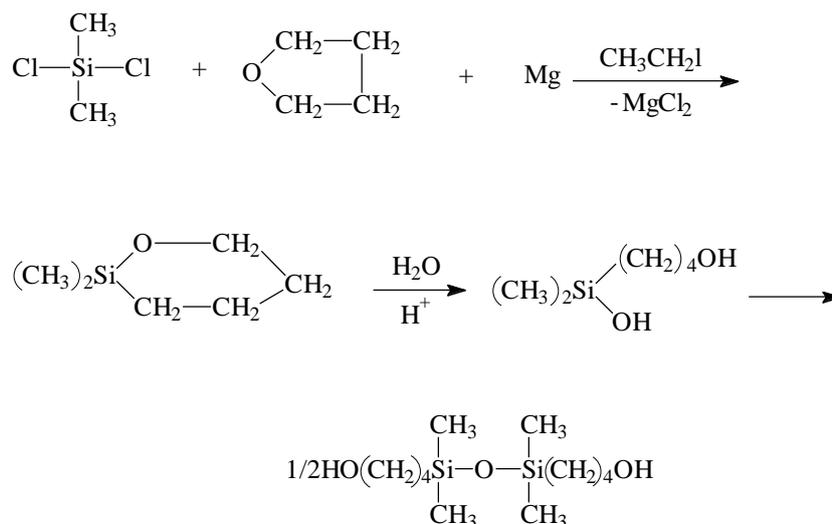
## EXPERIMENTAL

### Materials

Dimethyldichlorosilane and magnesium powder were purchased from State Medicine Group Chemical Reagents Co. Ltd., China. Dimethoxydimethyl silane, iodine, ethyl iodide, hydrochloric acid, diethyl ether, methanol, anhydrous magnesium sulphate, and sodium hydroxide were received from Liyang Tomorrow Chemical Industry Co., Shanghai Chemical Reagents Co. Ltd., Taicang Xinhua Chemical Plant, Wuhan Chemical Plant, Shanghai Malu Pharmacy Plant, Shanghai Zhenxing Chemical Reagents First Plant, Shanghai Shisi Hewei Chemical Industry Co. Ltd., and Tianjin Chemical Reagents Third Plant, China, respectively. Anhydrous sodium carbonate and anhydrous sodium bicarbonate were purchased from Shanghai Hongguang Chemical Plant, China. These reagents were used without further purification. Toluene (Beijing Yili Jingxi Chemical Reagents Co. Ltd., China) was distilled before use. Pyridine (Shanghai Chemical Reagents First Plant, China) and acetic anhydride (Tianjin Kelong Chemical Reagents Plant, China) were distilled under vacuum before use. Phenol phthalol was purchased from Shanghai San Aisi Reagents Co. Ltd., China. Tetrahydrofuran (THF) was dried using 4-Å molecular sieve, and then refluxed with sodium for about 6 h and then distilled at 65~66°C to obtain the purified THF.

### Synthesis of BHBTMDS

A 500-mL, three-necked, round-bottom flask [7] was taken out from air oven when hot. Under nitrogen purge, the flask was charged with 15 g (0.62 mol) of magnesium powder. After that flask became cold, the flask was equipped with a mechanical stirrer, a reflux condenser, and a thermometer. Then 225 mL of purified THF and 75 g (0.52 mol) of dimethyldichlorosilane were added. One milliliter of ethyl iodide and about ten particles of iodine were added, and the reaction was initiated (when the reaction did not start, then



**Scheme I.** Reaction employed in BHBTMDS preparation.

initiation started under heating). The initiating reaction continued at 70 ~ 71°C for about 2 h automatically. When the initiating reaction died down, the mixture was heated at 70°C for 2 h and then filtrated. The filter residue was washed with toluene thrice and filtered. The solvent and residual dimethyldichlorosilane were removed and the residue was hydrolyzed with 18 mL of distilled water and 0.4 mL of concentrated HCl, then the mixture was stirred for 48 h. The solution was extracted with 80 mL of 5% of sodium carbonate, and then the crude was separated from the aqueous layer and dried with anhydrous sodium carbonate and filtered. The residue was stripped under vacuum (1333 Pa) at 71°C to obtain BHBTMDS (25 g). The reaction scheme employed in the preparation of BHBTMDS is shown in Scheme I.

### Synthesis of HB-PDMS

A 250-mL, three-neck, round-bottom flask equipped with a reflux condenser was charged with 6.0 g (0.0216 mol) of BHBTMDS, 95.4 g (0.795 mol) of dimethoxydimethyl silane, 14.3 g (0.795 mol) of distilled water and 1.7 mL of concentrated HCl. The mixture was heated at 60°C for 1 h. Methanol was then distilled off. 55 Milliliter of 6 N HCl was added and the contents were refluxed for 4 h. The crude product was then separated from the aqueous layer. 50 Milliliter of diethyl ether was added and the solution was extracted with 50 mL of 5% of sodium bicarbonate twice and then with distilled water until the washings were neutral (pH = 7.0). The solution was dried

with anhydrous magnesium sulphate. Diethyl ether was distilled off and the residue was stripped under vacuum at 70~80°C for an hour. The purified product was added slowly to a mixture of equal weight of methanol/water (weight ratio 77.5/22.5) to remove lower molecular weight fractions, including cyclics. The bottom organic layer was separated. 50 Milliliter of diethyl ether was then added to the organic layer and the solution was dried with anhydrous magnesium sulphate and filtered. Diethyl ether was then removed and the residue was stripped under vacuum (0.5 torr) at 80°C to obtain the final product [6]. The reaction scheme employed in the preparation of HB-PDMS is shown in Scheme II.

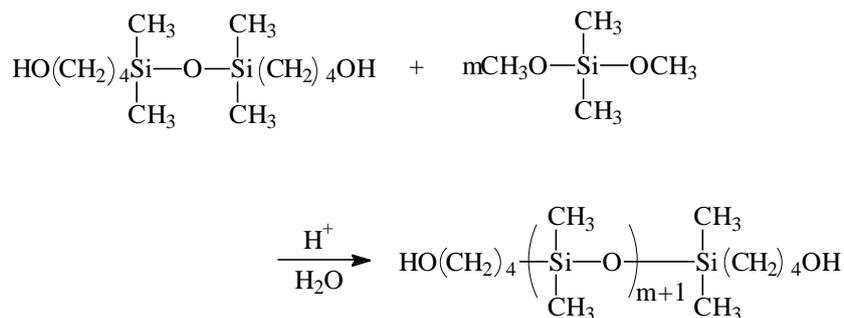
### Analytical Procedures

#### FTIR Microspectroscopic Analyses of BHBTMDS and HB-PDMS

FTIR Spectra of BHBTMDS and HB-PDMS (molar ratio 36.8:1 for dimethoxydimethyl silane:BHBTMDS) were obtained using a Nexus FTIR instrument (Thermo Nicolet Co., American) using solution cast films on KBr discs. All FTIR spectra were obtained in the wavenumber range from 500 to 4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ , and a minimum of 64 scans was signal-averaged at room temperature.

#### High-resolution $^1\text{H}$ NMR Analyses of BHBTMDS and HB-PDMS

$^1\text{H}$  NMR Spectra of BHBTMDS and HB-PDMS (molar ratio 36.8:1 for dimethoxydimethyl silane:



**Scheme II.** Reaction employed in HB-PDMS preparation.

BHBTMDS) were performed using a 400-MHz NMR spectrophotometer (Varian Co.).  $^1\text{H}$  NMR Spectra of 5% w/v deuterated-chloroform ( $\text{CDCl}_3$ ) solutions were obtained. Residual  $\text{CHCl}_3$  was used as an internal standard.

### End Groups Titration of HB-PDMSs

The number-average molecular weights were calculated based on hydroxyl numbers of macrodiols. The hydroxyl numbers of the purified and dried macrodiols were determined by an acetic anhydride reflux procedure.

A thoroughly dried, brown reagent bottle was charged with 100 mL of purified pyridine and 15 mL of purified acetic anhydride, and then the solution was mixing uniformly. A 100 mL, ground glass stopper [8] conical flask was charged with accurate weight of HB-PDMS (for example 1.0000 g) and 10 mL of so-called pyridine-acetic anhydride, and the flask neck was washed using minor pyridine. Then the flask was equipped with a reflux condenser and a drying tube. The contents were heated at  $100^\circ\text{C}$  for 1 h. After that, minor pyridine washed the reflux condenser. The reaction contents were then cooled to ambient temperature. Next, the contents were titrated with 1 N of NaOH until the neutral point, using 0.1% of phenol phthalol as the indicator. Blank titration was used as the same method. Each sample was titrated twice, and then the molecular weight of HB-PDMS was calculated.

## RESULTS AND DISCUSSION

### Synthesis of BHBTMDS

Figure 1 shows a typical FTIR microscopic spectrum of BHBTMDS recorded in the wavenumber range of

$500\sim 4000\text{ cm}^{-1}$ . Among FIIR absorption of BHBTMDS, four peaks at 3335, 2955, 2930, and  $2863\text{ cm}^{-1}$  are mainly caused by the alcoholic hydroxyl stretching vibration, the  $\text{CH}_3$  asymmetric stretching vibration, the  $\text{CH}_2$  asymmetric stretching vibration, and the  $\text{CH}_3$  symmetric stretching vibration, respectively. The peak at  $3335\text{ cm}^{-1}$  is the characteristic absorption peak of -OH group of alcoholic hydroxyl and silanol. Three peaks at 1252, 840, and  $790\text{ cm}^{-1}$  are mainly caused by Si- $\text{CH}_3$  stretching vibration,  $\text{CH}_3\text{-Si-CH}_3$  asymmetric deformation vibration, and  $\text{CH}_3\text{-Si-CH}_3$  symmetric deformation vibration, respectively. The presence of three peaks at 1252, 840, and  $790\text{ cm}^{-1}$ , accounts for Si having two methyl groups. The absorbance band at  $1410\text{ cm}^{-1}$  is caused by alcoholic hydroxyl in-plane bending vibration. The single absorbance band at  $1070\text{ cm}^{-1}$  is caused by Si-O-Si symmetric stretching vibration that is characteristic of a siloxane backbone. Its emergence indicates that the compound is disiloxane. The absorbance band at  $1176\text{ cm}^{-1}$  is caused by Si- $\text{C}_4\text{H}_8\text{OH}$  stretching vibration, and it emerges at the wavenumber range of  $1170\sim 1220\text{ cm}^{-1}$ . When the alkyl is longer, the peak removes to lower frequency region. The absorbance band at  $1176\text{ cm}^{-1}$  indicates that the alkyl on Si is long.

High-resolution  $^1\text{H}$  NMR spectrum for BHBTMDS is taken to help identify the structure. The high-resolution  $^1\text{H}$  NMR spectrum of BHBTMDS is provided in Figure 2. Those peaks at 0.06, 0.57, 1.23, 1.40, 1.61, and 3.66 ppm are chemical shifts of  $\text{H}_5$ ,  $\text{H}_1$ ,  $\text{H}_2$ ,  $\text{H}_3$ ,  $\text{H}_4$ , and -OH (Figure 2), respectively. Si only affects the chemical shift of  $\text{H}_5$ ; therefore its chemical shift is smallest. The chemical shift of  $\text{H}_1$  is affected by not only Si but also adjacent alkyl group; therefore its chemical shift is bigger than that of  $\text{H}_5$  and smaller than those of  $\text{H}_2$ ,  $\text{H}_3$ , and  $\text{H}_4$ . The chem-

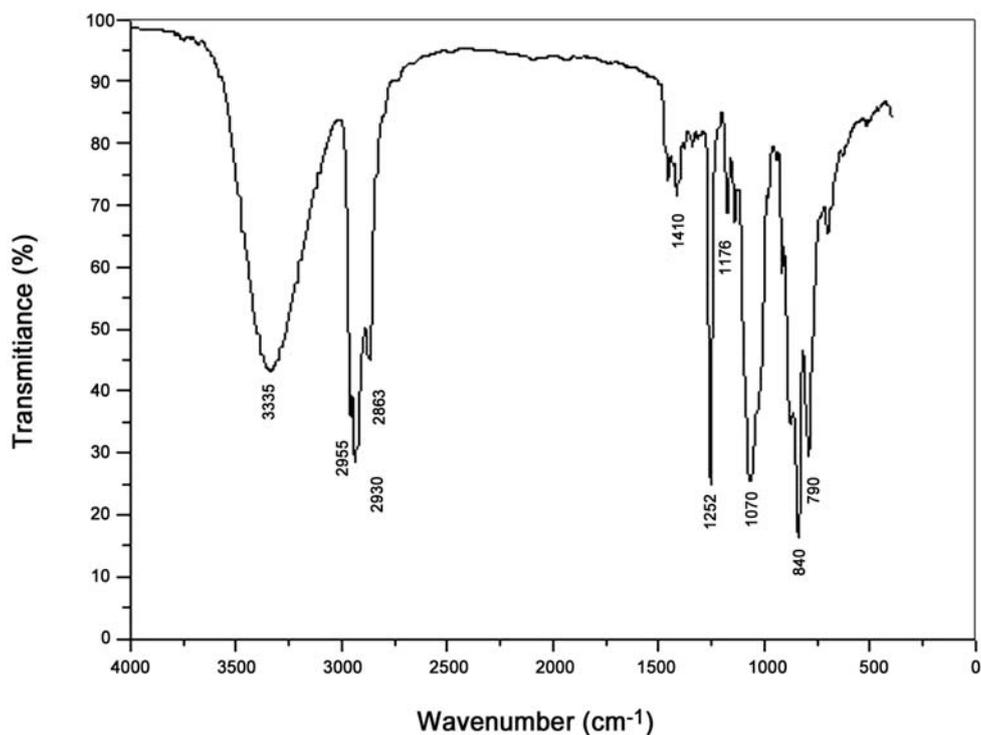


Figure 1. FTIR Microspectroscopic spectrum of BHBTMDS.

ical shift of H<sub>4</sub> is affected by not only -OH but also adjacent alkyl group; therefore its chemical shift is bigger than those of H<sub>1</sub>, H<sub>2</sub>, H<sub>3</sub>, and H<sub>5</sub>. Because the proton associated with the hydroxyl is active, its

chemical shift is biggest.

**Synthesis of HB-PDMS**

FTIR Spectrum of HB-PDMS (molar ratio 36.8:1 for

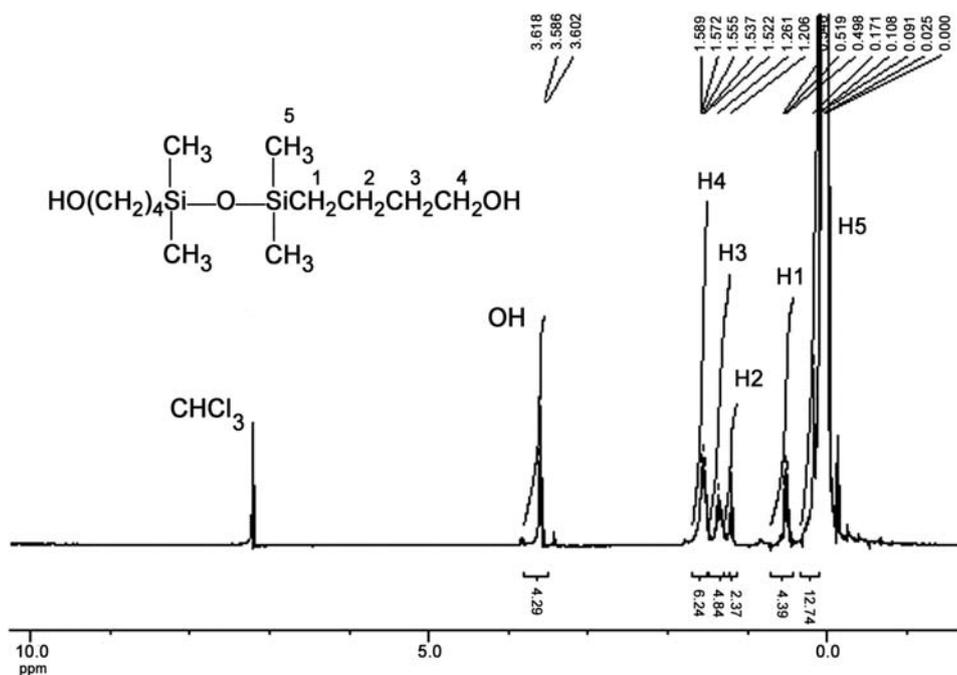


Figure 2. <sup>1</sup>H NMR Spectrum of BHBTMDS.

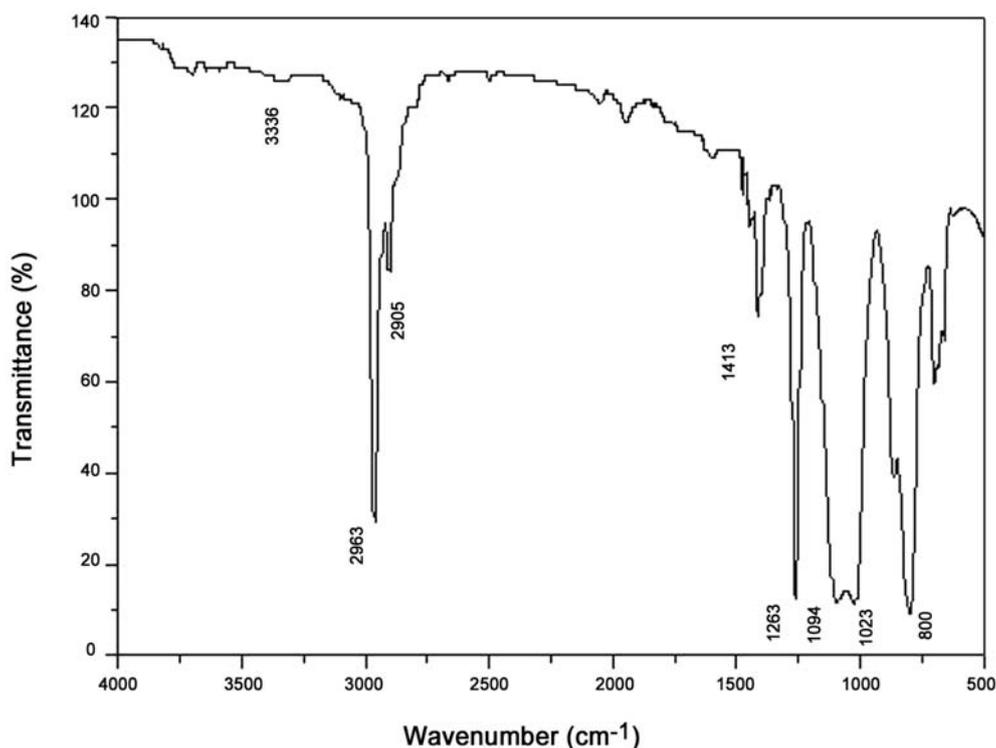


Figure 3. FTIR Microscopic spectrum of HB-PDMS.

dimethoxydimethyl silane:BHBTMDS) is shown in Figure 3. This figure shows a strong Si-O-Si stretching absorption at 1023 and 1094  $\text{cm}^{-1}$ , that is a characteristic peak of a siloxane backbone [9]. The spectral feature of greatest interest is that the characteristic peak splits or separates two peaks, indicating the compound is polysiloxane. Three peaks at 3336, 2963, and 2905  $\text{cm}^{-1}$  are mainly caused by the alcoholic hydroxyl stretching vibration, the  $\text{CH}_3$  stretching vibration, and the  $\text{CH}_2$  stretching vibration, respectively. The absorbance band at 1413  $\text{cm}^{-1}$  is caused by alcoholic hydroxyl in-plane bending vibration. In addition,  $\text{CH}_3$  bending and rocking peaks are observed at 1263  $\text{cm}^{-1}$  and 800  $\text{cm}^{-1}$ , respectively.

The high-resolution  $^1\text{H}$  NMR spectrum of HB-PDMS (molar ratio 36.8:1 for dimethoxydimethyl silane:BHBTMDS) is provided in Figure 4.  $^1\text{H}$  NMR Spectrum confirms the structure of  $\alpha,\omega$ -bis(4-hydroxy butyl) polydimethylsiloxane. Because the protons of HB-PDMS are similar to those of BHBTMDS, therefore the analytic procedure is similar to that of BHBTMDS. The difference in these two spectra allows us to assign methyl attached to Si peaks. The results from

FTIR and high-resolution  $^1\text{H}$  NMR clearly illustrate the successful synthesis of HB-PDMS.

#### End Group Titration of HB-PDMSs

The six samples of HB-PDMSs showed in Table 1 were prepared by using dimethoxydimethyl silane and BHBTMDS as reagents. In general, using the end group titration method, the number-average molecular weight of HB-PDMS obtained is higher than the targeted number-average molecular weight. This is due to [6] the fact that the methanol/water extraction of the

Table 1. Number-average molecular weight ( $M_n$ ) determinations of HB-PDMSs.

Sample No	Targeted $M_n$	$M_n$ by titration analysis
1	1000	2682±64
2	2000	3133±32
3	3500	3525±15
4	5000	6144±50
5	8000	8030±28
6	10000	10268±155

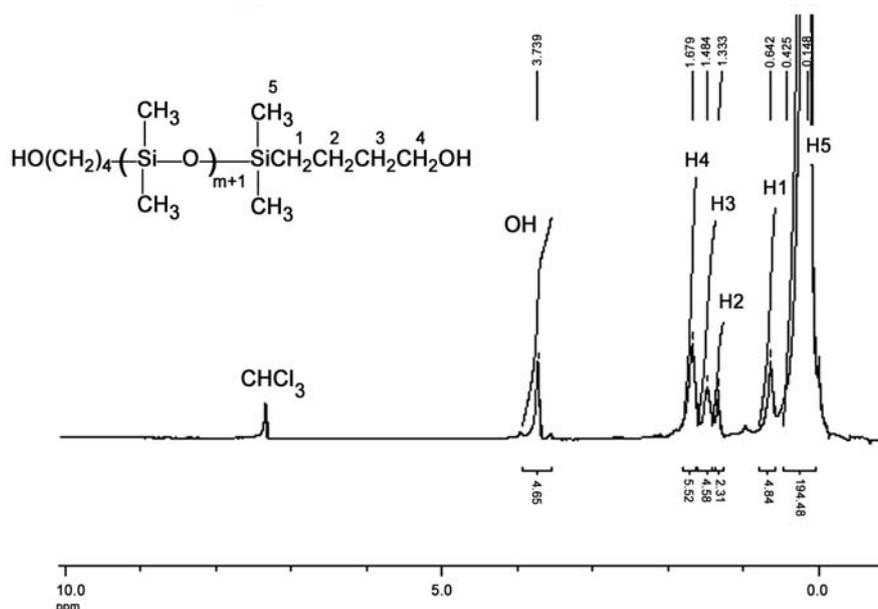


Figure 4.  $^1\text{H}$  NMR Spectrum of HB-PDMS ( $M_n=3525$ ).

crude product automatically caused a loss in the low molecular weight fractions of the product. When the molecular weight is lower, the deviation between targeted number-average molecular weight and experimented number-average molecular weight determined by end group titration is larger. At number-average molecular weight higher than 5,000 g/mol smaller increasing deviation is observed.

## CONCLUSION

BHBTMDS could be synthesized using dimethyldichlorosilane, purified tetrahydrofuran, and magnesium powder as the starting materials, and iodine and ethyl iodide as catalysts. The structure of BHBTMDS is characterized by FTIR spectroscopy and high-resolution  $^1\text{H}$  NMR. HB-PDMSs could be prepared, with good control of number-average molecular weight, by an equilibration reaction of dimethoxydimethyl silane and BHBTMDS in a stoichiometric amount of water and hydrochloric acid. The structure of HB-PDMS is also characterized by FTIR and high-resolution  $^1\text{H}$  NMR. The number-average molecular weights of HB-PDMSs can be determined successfully by end group titration method. The number-average molecular weight of HB-PDMS obtained is higher than the targeted molecular weight.

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