

# Synthesis and Characterization of $\alpha$ -Butyl-omega-{3-[2-hydroxy-3-(*N*-methyl-*n*-hydroxyethylamino)propoxy]propyl}polydimethylsiloxane

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Received 31 March 2009; accepted 23 August 2009

DOI 10.1002/app.31339

Published online 26 March 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A novel synthesis path for the monotelechelic polydimethylsiloxane with a diol-end group,  $\alpha$ -butyl-omega-{3-[2-hydroxy-3-(*N*-methyl-*N*-hydroxyethylamino)propoxy]propyl}polydimethylsiloxane, is described in this article. The preparation included three steps, which were anionic ring-opening polymerization, hydrosilylation, and epoxy addition. The structure and polydispersity index of the products were analyzed and confirmed by FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, H—H, and C—H.

Correlated Spectroscopy and gel permeation chromatography. The results demonstrated that each step was successfully carried out and the targeted products were accessed in all cases. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 882–887, 2010

**Key words:** epoxy addition;  $\alpha$ -butyl-omega-{3-[2-Hydroxy-3-(*N*-methyl-*N*-hydroxyethylamino)propoxy] propyl}polydimethylsiloxane; FTIR; NMR

## INTRODUCTION

Polydimethylsiloxane (PDMS) possess many unique properties, such as the extremely low glass transition temperature, low surface tension and surface energy, and low solubility parameter. In addition, PDMS are transparent to visible and UV light, very resistant to ozone and corona discharge, stable against atomic oxygen and even oxygen plasmas. Moreover, these properties show only a very small variation over a wide temperature range.<sup>1</sup> So it is the most important in terms of commercial applications. Block and graft copolymers consisting of PDMS as a segment component have gained increasing attention owing to the unique properties of these hybrid polymers both in bulk and at the surface.<sup>2</sup> Interest in the synthesis of PDMS-containing block and graft copolymers arises from two aspects: one is to obtain new PDMS-based materials with enhanced mechanical properties by introduction of the other component, and the other is to install the inherent characteristics of PDMS into another polymer.<sup>3</sup>

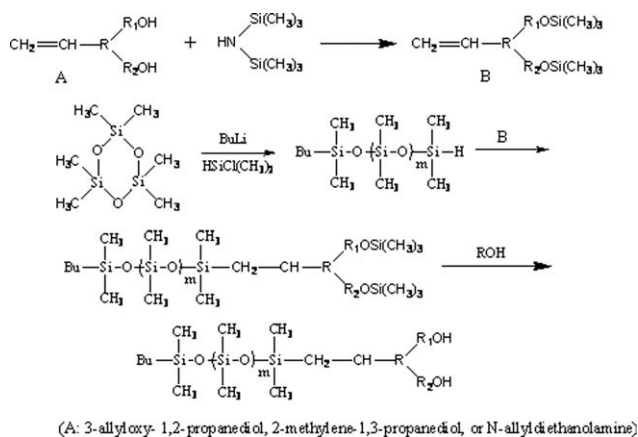
For the former, many researches have been focused on block copolymerization modification,

while in contrast, relatively scarce attention was put on graft copolymerization modification, especially the synthesis and characterization of PDMS with a diol group at only one chain end have been rare. To attain sufficient modification of surface properties of the final resin, the siloxane compound should be used in a considerably large proportion on block copolymerization modification.<sup>4</sup> So understanding the synthesis and characterization of PDMS with a diol group at one end of the chain is a matter of primary importance for studying and using them in the modification of organic polymers. The traditional methodologies<sup>4–6</sup> (Scheme 1) to synthesize PDMS with a diol group at only one chain end varied, but they include the same five steps, which are synthesizing or purchasing unsaturated allyl compounds with a diol end group, hydroxyl-protection, anionic ring-opening polymerization, hydrosilylation, and deprotection. We can see that these methodologies are complicated and some compounds are difficult to synthesize. The last step of deprotection of the silylated alcohols by acetic acid in ROH has one main drawback, namely the possible cutting of the PDMS chains to reform octamethyltetra-cyclosiloxane (D<sub>4</sub>).

In this article, with the purpose to prepare modified waterborne polymers with improved performance, a new approach (Scheme 2 and Scheme 3) to synthesize PDMS with a diol group at only one chain end was introduced. The preparation included three steps, which were anionic ring-opening

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Contract grant sponsor: Natural Science Foundation of Shandong Province; contract grant number: Y2006B22.



**Scheme 1** Synthesis of PDMS with a diol end group.

polymerization, hydrosilylation, and epoxy addition. The structure and polydispersity index of the products were analyzed and confirmed by FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, H—H, and C—H Correlated Spectroscopy (COSY) and gel permeation chromatography. The results demonstrated that each step was successfully carried out and the targeted products were accessed in all cases. It is found that the materials used in the experiment are easy to attain, and the new approach is easier than those used in the previous studies,<sup>4–6</sup> which involve hydroxyl protection and deprotection.

## EXPERIMENTAL

### Materials and methods

N-Methylmonoethanolamine (MMEA) and ally glycidyl ether (AGE), all industrial grade, were purchased from Changzhou Taihu Chemicals and Yudeheng, respectively. Toluene, ethanol, tetrahydrofuran (THF), all A.R. were products of Shanghai General Factory of Chemicals and Tianjin Dahua Chemicals. All these chemicals were distilled before use. Butyllithium (BuLi), dimethylchlorosilane (DMCS), and hexamethylcyclotrioxysilane ( $\text{D}_3$ ) were used as received without further purification.

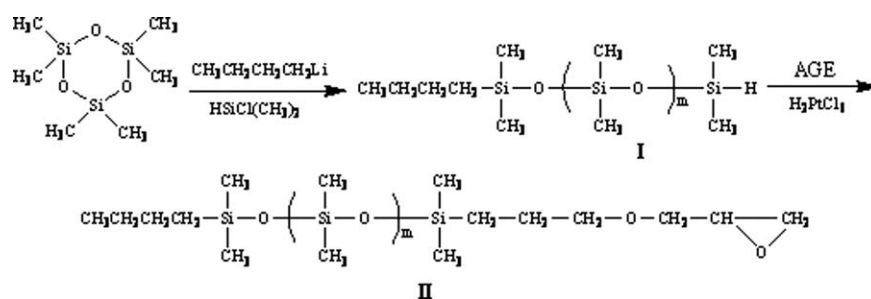
Fourier transform infrared spectra were recorded on a Nicolet FTIR Spectrometer Nexus 470 (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ). NMR Spectra were recorded on a Bruker AV600 NMR Spectrometer ( $^1\text{H}$ , 600 MHz,  $^{13}\text{C}$ , 150 MHz). Chemical shifts were reported in ppm and referenced to residual solvent resonances ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or an internal standard. The H—H COSY and C—H COSY techniques were also used to elucidate proton assignments of  $^1\text{H}$  NMR spectrum. GPC was performed with Waters 1525 Binary HPLC Pump using Waters 2414 Refractive Index Detector, Styragel HT 2, 3, 4 as columns, and THF as eluant.

### Synthesis of polydimethylsiloxane with Si-H end group I

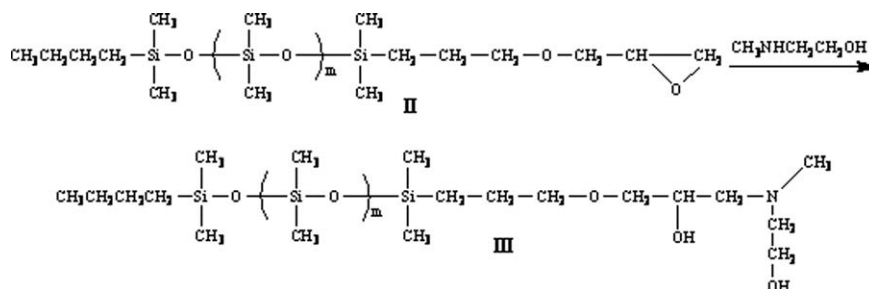
PDMS with Si—H end group was synthesized by anionic ring-opening polymerization of  $\text{D}_3$  as reported earlier.<sup>7</sup> A round-bottomed four-necked flask equipped with two funnels, a stirrer, a helium purge, was charged with 25 mL of toluene. 1.28 g (0.02 mol) of initiator, BuLi, was injected into the flask followed by drop-wise addition of 30 mL of tetrahydrofuran and the solution of 27.84 g (0.125 mol) of  $\text{D}_3$  and 30 mL of toluene. DMCS as end-capping agent was added into the reaction mixture after the mixture was stirred for 5 h. After the solvent and DMCS were evacuated under reduced pressure, the product was subjected to filtration to remove lithium chloride. Finally, H-containing silicone oil with certain molecular weight was obtained with a yield of 90%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 2962 (alkyl C—H stretching), 2127 (Si—H), 1261, 800 (Si—CH<sub>3</sub>), 1027–1092 (Si—O—Si).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz,  $\delta$ ppm): 0.11 (m, 122H, —Si(CH<sub>3</sub>)<sub>2</sub>), 0.44–0.48 (t, 2H, —Si—CH<sub>2</sub>), 0.79–0.83 (t, 3H, CH<sub>3</sub>—CH<sub>2</sub>), 1.23–1.24 (m, 4H, —(CH<sub>2</sub>)<sub>2</sub>—CH<sub>3</sub>), 4.63 (s, 1H, —Si—H).

### Synthesis of $\alpha$ -butyl-omega-[3-(2,3-epoxypropoxy)propyl]polydimethylsiloxane II

As previously reported in the literatures,<sup>8,9</sup> a round bottomed flask equipped with a thermometer, a stirrer, a nitrogen purge, and a reflux condenser (the



**Scheme 2** Synthesis of compound I and II.



Scheme 3 Synthesis of compound III.

later equipped with a tubular dryer filled with anhydrous calcium chloride), was charged consecutively with excessive AGE, toluene (40 mL) and chloroplatinic acid solution (2% in isopropanol, 300  $\mu\text{L}$ ). The flask was heated to 90°C followed by drop-wise addition of 7.33 g (4.86 mmol) of product I. The reaction mixture was kept at this temperature for 8 h. Toluene and excessive AGE were removed under vacuum. Then the product II was filtrated with a yield of 89%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3048 (epoxy group  $\text{---CH}_2\text{---}$  asymmetrical stretching), 2962 (alkyl C—H stretching), 1260, 800 ( $\text{Si---CH}_3$ ), 1023–1093 ( $\text{Si---O---Si}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz,  $\delta$ ppm):

0.11 (m, 122H,  $\text{---Si}(\text{CH}_3)_2$ ), 0.46–0.48 (m, 4H,  $\text{Si---CH}_2$ ), 0.79–0.82 (t, 3H,  $\text{CH}_3\text{---CH}_2$ ), 1.23–1.24 (m, 4H,  $\text{---}(\text{CH}_2)_2\text{---CH}_3$ ), 1.52–1.56 (m, 2H,  $\text{Si---CH}_2\text{---CH}_2$ ), 2.53 and 2.72 (m, 2H,  $\text{CH---CH}_2\text{O}$ ), 3.07 (m, 1H,  $\text{CH---CH}_2\text{O}$ ), 3.30–3.48 and 3.56–3.64 (m, 2H,  $\text{O---CH}_2\text{---CH}$ ), 3.37–3.43 (m, 2H,  $\text{CH}_2\text{---O---CH}_2$ ).

#### Synthesis of $\alpha$ -butyl-omega-[3-[2-hydroxy-3-(*N*-methyl-*N*-hydroxyethylamino)propoxy]propyl]Poly dimethylsiloxane III

Product II (5.51 g, 3.39 mmol), MMEA (4.07 g, 0.05 mol), and ethanol (35 mL) were charged into three-

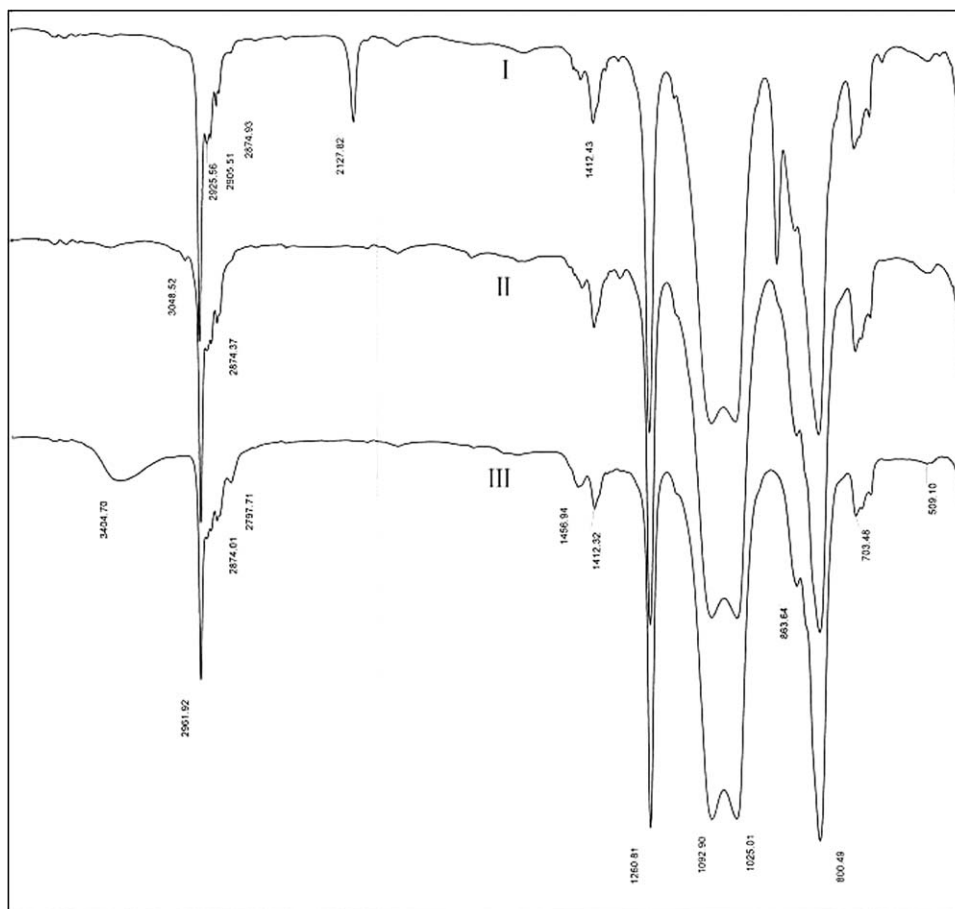


Figure 1 IR spectra of compound I, II, and III.

necked flask equipped with thermometer, condenser, and magnetic stirrer. The reaction mixture was stirred at 70°C for 10 h. Excessive ethanol and MMEA were removed under reduced pressure. The product **III** was obtained with a yield of 90%, PDI = 1.17. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3404 ( $-\text{OH}$  stretching), 2962 (alkyl  $\text{C}-\text{H}$  stretching), 1261, 800 ( $\text{Si}-\text{CH}_3$ ), 1025–1093 ( $\text{Si}-\text{O}-\text{Si}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz,  $\delta$ , ppm): 0.11 (m, 122H,  $-\text{Si}(\text{CH}_3)_2$ ), 0.52–0.54 (m, 4H,  $\text{Si}-\text{CH}_2$ ), 0.86–0.88 (t, 3H,  $\text{CH}_3-(\text{CH}_2)_2$ ), 1.30–1.32 (m, 4H,  $-(\text{CH}_2)_2-\text{CH}_3$ ), 1.58–1.62 (m, 2H,  $\text{Si}-\text{CH}_2-\text{CH}_2$ ), 2.32 (s, 3H,  $\text{N}-\text{CH}_3$ ), 2.53–2.56 and 2.64–2.66 (m, 2H,  $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 2.57–2.59 (m, 2H,  $\text{CH}(\text{OH})-\text{CH}_2$ ), 3.38–3.48 (m, 4H,  $\text{CH}_2-\text{O}-\text{CH}_2$ ), 3.63–3.64 (m, 2H,  $\text{CH}_2-\text{OH}$ ), 3.91 (m, 1H,  $\text{CH}(\text{OH})$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz,  $\delta$ , ppm): 1.04 (C-4), 13.82 (C-4), 14.08 (C-3'), 17.93 (C-3), 23.34 (C-5), 25.43 and 26.37 (C-2), 42.66 (C-11), 59.11 (C-10), 59.57 (C-9), 60.22 (C-8), 67.65 (C-7), 73.04 (C-6), 74.40 (C-6').

## RESULTS AND DISCUSSION

### Synthesis and characterization of compound I and II

PDMS with  $\text{Si}-\text{H}$  end group, compound **I**, was prepared by end-capping the anionic ring-opening polymerization of  $\text{D}_3$  initiated with  $\text{BuLi}$ <sup>7</sup> as shown in Scheme 2. The reaction product was subjected to IR and  $^1\text{H}$  NMR analysis (Figs. 1 and 2). The characteristic of IR spectrum of compound **I** was that the emergence of  $\text{Si}-\text{H}$  and  $\text{Si}-\text{O}-\text{Si}$  bands at 2127  $\text{cm}^{-1}$  and 1027–1092  $\text{cm}^{-1}$ , respectively.  $^1\text{H}$  NMR spectrum of compound **I** also revealed that the peak at 4.63 ppm was assigned to the  $\text{Si}-\text{H}$  group and corresponding peak assignments are given in the spectrum.

We know that the  $\text{Si}-\text{H}$  group can undergo the hydrosilylation reaction to add to unsaturated allyl compounds,  $\alpha$ -butyl-omega-[3-(2,3-epoxypropoxy)propyl]polydimethylsiloxane, compound **II**, was synthesized via hydrosilylation reaction between

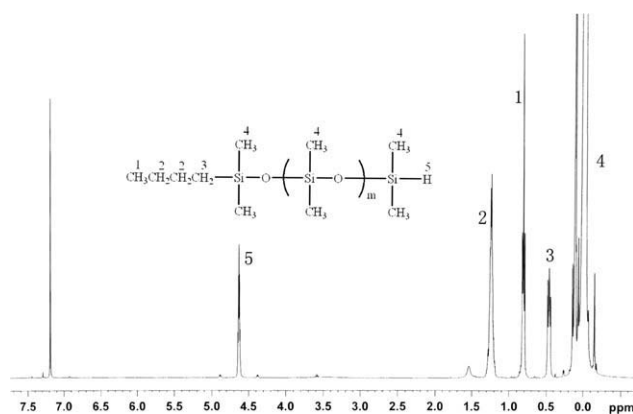


Figure 2  $^1\text{H}$  NMR spectrum of compound **I**.

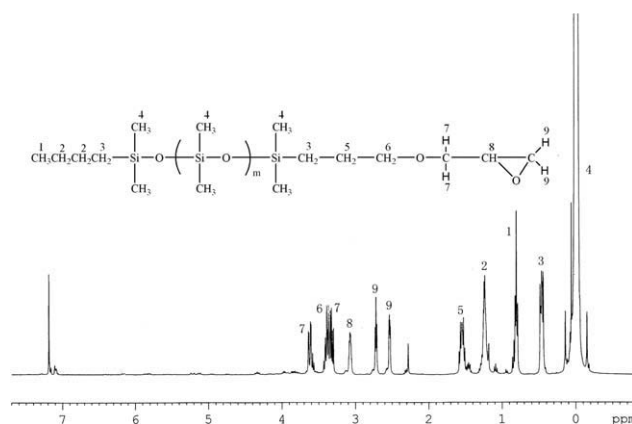


Figure 3  $^1\text{H}$  NMR spectrum of compound **II**.

AGE and compound **I** as depicted by Scheme 2. Comparing with the spectra of compound **I** and AGE, IR Spectrum of compound **II** (Fig. 1) showed the complete disappearance of  $\text{Si}-\text{H}$  vibration and  $\text{C}=\text{C}$  double bond vibration, which were observed at 2127  $\text{cm}^{-1}$  and 1642  $\text{cm}^{-1}$  in the spectra of PDMS with  $\text{Si}-\text{H}$  end group and AGE, and appearance of a weak epoxy vibration peak appeared at 3049  $\text{cm}^{-1}$ . This indicated that hydrosilylation reaction had happened between  $\text{C}=\text{C}$  double bond and  $\text{Si}-\text{H}$  group. Meanwhile the data of  $^1\text{H}$  NMR spectrum of hydrosilylation product **II** (Fig. 3) including chemical shifts and peak area integrations also validated the occurrence of hydrosilylation reaction. In the spectrum, corresponding peak assignments of compound **II** are given.

### Synthesis and characterization of compound III

With the object of preparing and isolating  $\alpha$ -butyl-omega-[3-[2-hydroxy-3-(*N*-methyl-*N*-hydroxyethylamino)propoxy]propyl]Polydimethylsiloxane, compound **III**, the reaction shown in Scheme 3 was carried out using MMEA and compound **II**. The epoxy addition reaction had happened between epoxy group and  $\text{N}-\text{H}$  bond to obtain a diol group.

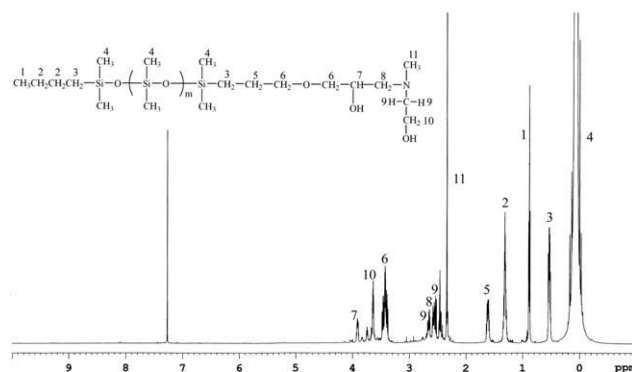


Figure 4  $^1\text{H}$  NMR spectrum of compound **III**.

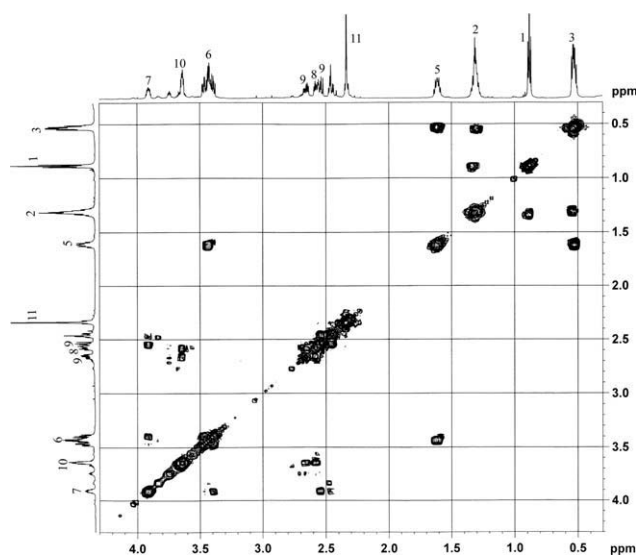


Figure 5 H—H COSY spectrum of compound III.

Figure 1 shows the IR spectrum of compound III. In comparison with the spectra of the reacting materials, the spectrum of compound III exhibits the following characteristics: (1) Complete disappearance of epoxy vibration, which was observed in the compound II spectrum at  $3049\text{ cm}^{-1}$ ; (2) Appearance of  $\text{—OH}$  group at  $3404\text{ cm}^{-1}$  due to its stretch vibration; (3) Other peaks, i.e.  $\text{Si—O—Si}$  stretching vibration at  $1025\text{--}1093\text{ cm}^{-1}$ ,  $\text{Si—CH}_3$  bending vibration at  $1261\text{ cm}^{-1}$  and its swing vibration at  $800\text{ cm}^{-1}$ , are also observed. This confirms the formation of compound III through the epoxy addition reaction.

This compound III was then subjected to  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis. The  $^1\text{H}$  NMR spectrum is shown in Figure 4. From the chemical shifts and the peak area integrations, the peaks representing protons labeled on the molecular formula are assigned in the spectrum. The signals due to the  $\text{N—CH}_3$  protons at 2.32 ppm and the  $\text{—CH(OH)}$  proton at 3.91 ppm were observed and other chemical shifts for protons labeled 1–5 show only limited variations comparing with the spectrum of compound II, indicating that

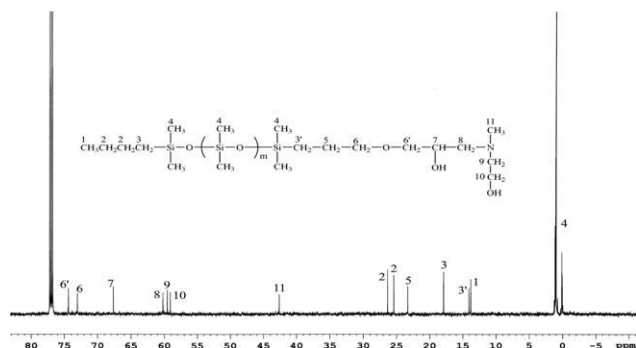


Figure 6  $^{13}\text{C}$  NMR spectrum of compound III.

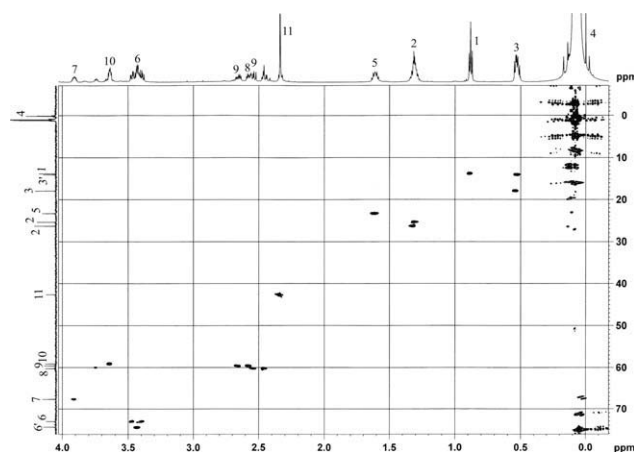


Figure 7 C—H COSY spectrum of compound III.

the epoxy addition reaction took place quantitatively. For more support the  $^1\text{H}$  NMR resonances assignments, a H—H COSY were conducted and the spectrum is given in Figure 5. As this H—H COSY reveals interaction and coupling effects between the adjacent protons, Figure 5 constitutes a reconfirmation to the above peak assignments. The  $^{13}\text{C}$  NMR spectrum of compound III is displayed in Figure 6. The chemical shifts for carbon labeled on the molecular formula are given in the spectrum, which agree with the chemical structure of compound III. The C—H COSY (Fig. 7) experience was then carried out, which correlates absorbance of proton with that of its bonding carbon atom as shown in Figure 7. The molecular weight of compound III was estimated (Table I) along with it obtained via GPC, functional group analysis (based on hydroxyl) as well as its theoretical values. The PDI of the product is 1.17. Significant discrepancy is revealed when the value obtained from GPC. This might be due to the fact that the polystyrene was used as the polymer standard in the test, which may lead to inaccurate results knowing that these two polymers are of very different natures.

## CONCLUSIONS

$\alpha$ -butyl-omega-[3-[2-hydroxy-3-(*N*-methyl-*N*-hydroxyethylamino)propoxy]propyl]Polydimethylsiloxane, a monotelechelic PDMS with a diol end group, which can modify other organic polymers by graft copolymerization can be prepared by anionic ring-opening polymerization, hydrosilylation and epoxy addition.

TABLE I  
Molecular Weight of Compound III

$\frac{M_n}{\text{Theo.}}$	$\frac{M_n}{\text{—OH}}$	$\frac{M_n}{^1\text{HNMR}}$	$\frac{M_n}{\text{GPC}}$	$\frac{M_w}{\text{GPC}}$	$\frac{M_w}{M_n}$
1689	1540	1711	2317	2709	1.17

The successful synthesis of this kind of compound is a matter of primary importance for researches on graft copolymerization.

### References

1. Iskender, Y.; James, E. M. *Adv Polym Sci* 1988, 86, 6.
2. Yasuyuki, T.; Akira, F.; Saeri, M.; Kiyokazu, I. *J Colloid Interface Sci* 1986, 114, 16.
3. Li, W. D.; Huang, B. T. *Makromol Chem* 1989, 190, 2373.
4. Hisao, M.; Takeshi, S.; Michio, Z. P. U.S. Pat. 5,059,707 (1991).
5. Ichinohe, Annaka-shi, Gunma-ken. EP 0356963, 1989.
6. Yu, Y. T.; Zhang, Q. S.; Zhang, M.; Sun, H. F. *J Appl Polym Sci* 2008, 109, 2576.
7. Hideki, K.; Yasuyuki, T.; Kiyokazu, I. *Polym J* 1987, 19, 1091.
8. Feng, S. Y.; Cui, M. Z. *J React Funct Polym* 2000, 45, 7983.
9. Zhu, X. L.; Zhang, M.; Zhang, Q. S.; Feng, S. Y.; Kong, X. Z. *Eur Polym J* 2005, 41, 1993.