Synthesis and Characterization of α-Butyl-ω-*N,N*-dihydroxyethylaminopropylpolydimethylsiloxane

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ABSTRACT: α-Butyl-ω-*N,N*-dihydroxyethylaminopropylpolydimethylsiloxane, a monotelechelic polydimethylsiloxane with a diol-end group, which is used to prepare polyurethane–polysiloxane graft polymer, was successfully synthesized. The preparation included five steps, which are hydroxyl protection, alkylation, anionic ring-opening polymerization, hydrosilylation, and deprotection. The products were characterized by FTIR, GC, LC-MS, ^{1}H NMR, and elemental analysis. The results showed that each step was successfully carried out and the targeted products were synthesized in all cases. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2576–2582, 2008

Key words: α-butyl-ω-*N,N*-dihydroxyethylaminopropylpolydimethylsiloxane; FTIR; NMR; polysiloxanes; ring-opening polymerization

INTRODUCTION

It is well known that polysiloxanes possess a variety of unique and superior properties, such as high- and low-temperature resistance, low surface energy, good water resistance, aging resistance, corrosion resistance, climate resistance, electric characteristics, good UV stability, physiological inertness, biocompatibility, and so on.[1,2] So polysiloxanes exhibit dual virtues of organic and inorganic materials. Copolymerization of polysiloxanes with reactive functional groups and other organic polymers can endow the organic polymers with the excellent properties of polysiloxanes so that new polymer materials with special properties can be obtained.[3–5] It is an effective way to advance mechanics performance of polysiloxanes and to introduce its virtues into other polymers. Difunctional polysiloxanes are often used for the synthesis of polyurethane–polysiloxane graft or block polymers. The difunctional hydroxyalkyl terminated polysiloxanes are especially useful to produce waterborne polyurethanes modified with polysiloxanes, particularly for preparation of aqueous polyurethane dispersion.

Therefore, many researches have been focused on block or graft copolymerization modification. Diol-terminated polydimethylsiloxanes synthesized via hydrosilylation reaction between a one-end-hydrogenated polydimethylsiloxane and unsaturated allyl compounds with a diol end group are very useful for preparing graft copolymers. However, studies on polydimethylsiloxanes with a diol end group, particularly with respect to the synthesis and characterization, have been rare. Hisao et al.[6] prepared 1-(2-hydroxymethyl-3-hydroxypropyl)-1,1,3,3,3-pentamethyldisiloxane via addition reaction between 1,1,3,3,3-pentamethyldisiloxane and 2-methylene-1,3-propanediol. But there are some difficulties in synthesizing 2-methylene-1,3-propanediol. Hideki et al.[7] synthesized a series of uniform-size polydimethylsiloxanes containing a silane end group with 3-allyloxy-1,2-propanediol (Scheme 1). However, the compound 3-allyloxy-1,2-propanediol has two hydroxyl groups at one end, of which one group is a primary hydroxyl group and the other is a secondary hydroxyl group. And these two hydroxyl groups have different reactivities from each other. Therefore, in this article, with the purpose to prepare polydimethylsiloxane with a diol end group having same reactivities, α-butyl-ω-*N,N*-dihydroxyethylaminopropylpolydimethylsiloxane which has two primary hydroxyl groups was prepared via a multistep procedure, which involves hydroxyl protection, alkylation, anionic ring-opening polymerization, hydrosilylation, and deprotection. And the targeted compounds were characterized through FTIR, GC, LC-MS, ^{1}H NMR, and elemental analysis. The results showed that each step was successfully carried out and the targeted products were accessed in all cases. Understanding the synthesis and characterization of polydimethylsiloxanes with a diol end group is a matter of primary

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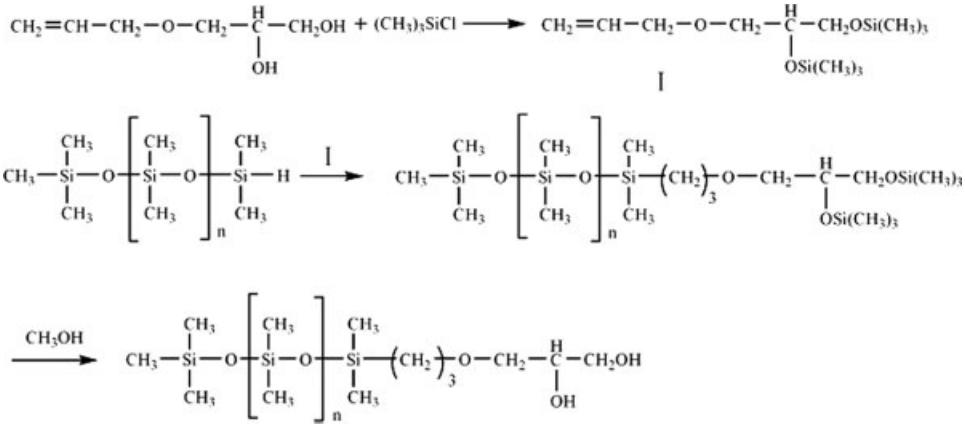


Scheme 1 Synthesis of PDMS with a diol end-group.

importance for studying and using them in the modification of organic polymers.

EXPERIMENTAL

Materials and methods

Hexamethyldisilazane and 3-bromopropene, all industrial grade, were purchased from Shanghai Huitian New Chemical Material and Zouping Mingxing Chemicals (Shanghai, China), respectively; toluene, methanol (Tianjin, China), and tetrahydrofuran, all A.R, were products of Shanghai General Factory of Chemicals and Tianjin Dahua Chemicals. All these chemicals were distilled before use. Butyllithium, dimethylchlorosilane, and hexamethylcyclotrisiloxane were used as received without further treatment.

Samples were cross-examined using different instruments combined with chemical analysis method. Infrared spectra were recorded on a Nicolet Tensor 470 FTIR Spectrometer (Nicolet, USA). ^{1}H NMR spectra were done at 27°C on a Bruker AVENCE 600 spectrometer (Bruker, Switzerland) with $CDCl_3$ as solvent and tetramethylsilane (TMS, δ = 0 ppm) as internal standard. Liqiud chromatography–mass spectrometer analyses were carried out on LTQ Orbitrap XL Hybride FT Mass Spectrometer (Thermo Fisher, USA). The mass spectrometer was operated in electron spray ionization (ESI) source at 275°C and in the positive ion full scanning mode with 100–2000 amu scan range.

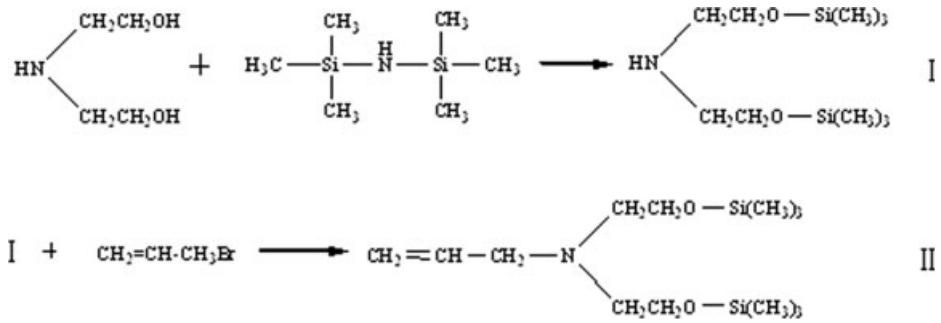
Bis(2-(trimethylsilyloxy)ethyl)amine and *N,N*-bis(2-(trimethylsilyloxy)ethyl)allylamine were detected using gas chromatography and liquid chromatography–mass spectrometer analyses. A capillary column (30.0 m × 0.32 mm × 0.5 μm) was used with nitrogen as the carrier. The column temperature profile was programmed with initial temperature at 100°C maintained for 2 min, followed by a constant increase to 200°C at 10°C/min and maintained at 200°C for 2 min. Injection port and FID detector temperature were set at 210 and 230°C, respectively.

Synthesis of bis(2-(trimethylsilyloxy)ethyl)amine I

About 90.50 g (0.56 mol) of hexamethyldisilazane was slowly added to 52.25 g (0.5 mol) of diethylolamine. The reaction was carried out in a 500-mL round-bottomed three-necked flask equipped with a magnetic stir bar, condenser, and thermometer.[6] The reaction mixture was stirred at reflux for 8 h, then the final mixture was vacuum-distilled under 5 mmHg and the distillate from 104 to 106°C was collected with a yield of 93%. IR (KBr, ν, cm^{-1}): 3337 (*N*—H), 1251, 841 (Si—CH_3), 1100 (Si—O—C). ^{1}H NMR ($CDCl_3$, 600 MHz, δ ppm): 0.03–0.22 (m, 18H, Si—CH_3), 1.83 (s, 1H, NH), 2.73–2.75 (t, 4H, *N*—CH_2), 3.69–3.71 (t, 4H, O—CH_2). Purity: 98%. Elemental analysis calcd. for $C_{10}H_{27}Si_2O_2N$ (%): C 48.19, H 10.84, N 5.62, O 12.85. Found: C 48.13, H 10.86, N 5.68, O 12.61. MS (ESI, 70 eV): *m/z* (%) = 250.1648 (100) $[M + H]^+$.

Synthesis of *N,N*-bis(2-(trimethylsilyloxy)ethyl)allylamine II

About 24.90 g (0.10 mol) of above product was prelocated into a round-bottomed flask, and then 6.05 g (0.05 mol) of 3-bromopropene was added into the flask under agitation. The reaction solution was stirred at 5°C for 1 h, followed by filtration to remove the ammonium. The alkylation product was separated through distillation under reduced pressure (5 mmHg) from the filtrate above, and the distillate between 118 and 120°C was collected as a colorless liquid. IR (KBr, ν, cm^{-1}): 3078 (=C—H), 1642 (C=C), 1251, 841 (Si—CH_3), 1096 (Si—O—C), 996, 919 (=C—H). ^{1}H NMR ($CDCl_3$, 600 MHz, δ ppm): 0.07–0.22 (m, 18H, Si—CH_3), 2.65–2.69 (t, 4H, *N*—CH_2), 3.19–3.22 (t, 2H, *N*—CH_2—CH=CH_2),



Scheme 2 Syntheses of compounds **I** and **II**.

3.63–3.65 (t, 4H, O—CH_2), 5.12–5.19 (m, 2H, =CH_2), 5.82–5.89 (m, 1H, =CH). Purity: 97%. Elemental analysis calcd. for $C_{13}H_{31}Si_2O_2N$ (%): C 53.98, H 10.73, N 4.84, O 11.07. Found: C 53.88, H 10.72, N 4.87, O 11.13. MS (ESI, 70 eV): *m/z* (%) = 290.1956 (100) $[M + H]^+$.

Synthesis of H-containing silicone oil III

As previously reported in the literature,[8] a round-bottomed four-necked flask, equipped with two funnels, a stirrer, a helium purge, was charged with 25 mL of toluene. 1.92 g (0.03 mol) of initiator, butyllithium, was injected into the flask, followed by dropwise addition of 30 mL of tetrahydrofuran and the solution of 26.52 g (0.105 mol) of D_3 and 30 mL of toluene. Dimethylchlorosilane as end-capping agent was added into the reaction mixture after the mixture was stirred for 5 h. Toluene and tetrahydrofuran were removed under reduced pressure; the product was subjected to filtrate to remove lithium chloride. H-containing silicone oil with certain molecular weight was obtained with a yield of 92%. IR (KBr, ν, cm^{-1}): 2128 (Si—H), 1261, 841 (Si—CH_3), 1093 (Si—O—Si). ^{1}H NMR ($CDCl_3$, 600 MHz, δ ppm): 0.01–0.08 (m, 80H, Si—CH_3), 0.44–0.46 (t, 2H, Si—CH_2), 0.81–0.83 (t, 3H, CH_3—CH_2), 1.21–1.24 (t, 4H, $(CH_2)_2$—CH_3), 4.63 (m, 1H, Si—H).

Synthesis of α-butyl-ω-*N,N*-bis (2-(trimethylsilyloxy)ethyl) aminopropylpolydimethylsiloxane IV

According to the literature[9,10] reported previously, a round-bottomed flask, equipped with a stirrer, a thermometer, a nitrogen purge, and a reflux condenser (the later equipped with a tubular dryer filled with anhydrous calcium chloride), was charged with excessive product **II**, 25 mL of toluene, and 40 μL of chloroplatinic acid solution (2% in isopropanol). The flask was heated to 90°C, followed by dropwise addition of 8.25 g (8.40 mmol) of product **III**, and kept at this temperature for 8 h. Toluene and excessive product **II** were removed under vacuum. The hydrosilylation product was obtained with a yield of 80%. ^{1}H NMR ($CDCl_3$, 600 MHz, δ ppm): 0.02–0.22 (m, 98H, Si—CH_3), 0.44–0.48 (m, 4H, Si—CH_2), 0.79–0.82 (m, 3H, CH_3—$(CH_2)_2$), 1.23–1.24 (m, 4H, $(CH_2)_2$—CH_3), 1.49–1.52 (m, 2H, Si—CH_2—CH_2), 2.42–2.49 (t, 2H, *N*—CH_2), 2.56–2.58 (t, 4H, N—$(CH_2$—$CH_2)_2$), 3.52–3.56 (t, 4H, O—$(CH_2$—$CH_2)_2$).

Synthesis of α-butyl-ω-*N,N*-dihydroxyethylamino propylpolydimethylsiloxane V

About 8.00 g (6.29 mmol) of hydrosilylation product and 67.12 g of methanol were charged into three-necked flask equipped with thermometer, condenser and magnetic stir, followed by addition of 0.1 mL of acetic acid as catalyst.[11] The reaction mixture was stirred at reflux for 15 h. Acetic acid was then neutralized by adding 1 mL of potassium hydroxide methanol solution (1 mol/L). Methanol and substances with low boiling point were removed by vacuum and the deprotection product was obtained with a yield of 82%. ^{1}H NMR ($CDCl_3$, 600 MHz, δ ppm): 0.01–0.22 (m, 98H, Si—CH_3), 0.44–0.48 (m, 4H, Si—CH_2), 0.79–0.82 (m, 3H, CH_3—$(CH_2)_2$), 1.23–1.24 (m, 4H, $(CH_2)_2$—CH_3), 1.55–1.59 (m, 2H, Si—CH_2—CH_2), 1.94 (s, 2H, OH), 2.73–2.76 (t, 2H, *N*—CH_2), 2.89–2.91 (t, 4H, N—$(CH_2$—$CH_2)_2$), 3.54–3.56 (t, 4H, O—$(CH_2$—$CH_2)_2$).

RESULTS AND DISCUSSION

Syntheses and characterization of compounds I and II

Bis(2-(trimethylsilyloxy)ethyl)amine and *N,N*-bis(2-(trimethylsilyloxy)ethyl)allylamine were prepared via hydroxyl protection and alkylation reaction as depicted by Scheme 2. Diethylolamine was first protected by hexamethyldisilazane via hydroxyl protection, particularly because dehydrogenation reaction can occur between hydroxyl group and Si—H group of H-containing silicone oil. On the other hand, if alkylation reaction between diethylolamine and 3-bromopropene was first carried out, there exist a lot of

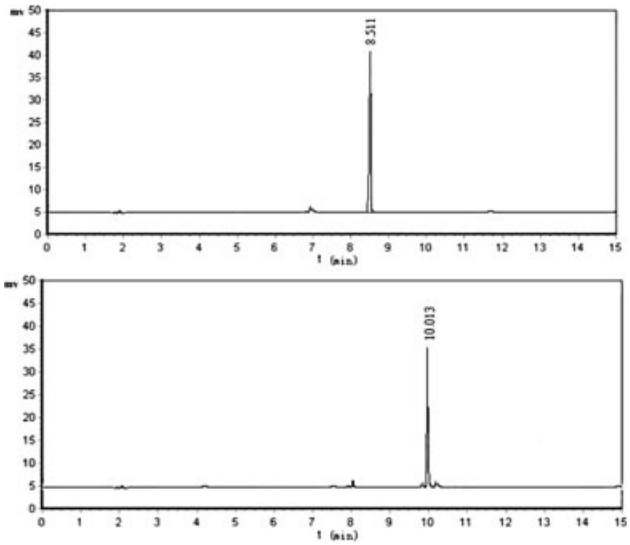


Figure 1 GC spectra of compounds **I** and **II**.

difficulties in filtrating to remove the ammonium salt. In contrast, when hydroxyl protection occurred before alkylation reaction, the boiling point and viscosity of hydroxyl protection product were reduced so that the product was easy to be separated and purified. When utilizing GC to follow the reaction process, GC showed that there was an unknown peak whose retention time was at 8.5 min (Fig. 1). In comparison with the retention time of reactants, we supposed that the peak at 8.5 min was the peak of hydroxyl protection product. To validate our guess, the product was separated under vacuum and subjected to characterization. Its refractive index was measured as being n_D^{25} = 1.4196. The product was subjected to IR analysis. IR spectrum of the product which was presented in Figure 2 showed that there was a weak amino vibration peak at 3337 cm^{-1}. And Si—CH_3 vibration and Si—O—C vibration peaks were also observed in the spectrum of the compound **I**. And then the compound was subjected to ^{1}H NMR analysis. ^{1}H NMR spectrum (Fig. 3) revealed that there were four peaks which are easily recognized from the chemical shifts and the peak area integrations.

In the second step, the GC spectrum of the filtrate displayed another manifest peak with retention time at 10 min. The product, assumingly the alkylation product **II**, was also separated under vacuum and its refractive index was n_D^{25} = 1.4292. The product was first subjected to IR analysis. Comparing with the spectrum of compound **I**, the spectrum of compound **II** exhibited the following main characteristics: A weak amino vibration peak disappeared completely at 3337 cm^{-1} and C=C double bond vibration appeared at 1642 cm^{-1}. And other peaks, Si—CH_3 vibration and Si—O—C vibration, were

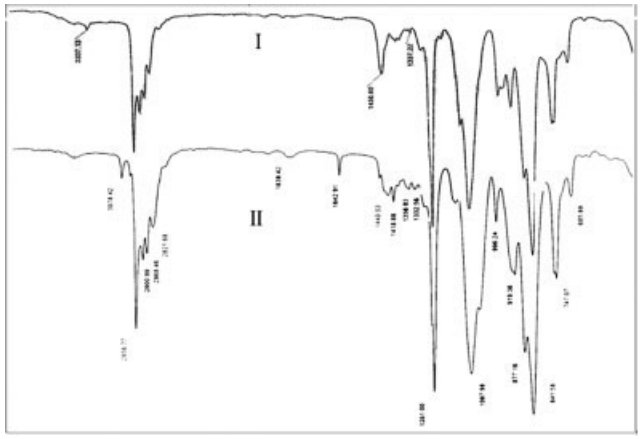


Figure 2 IR spectra of compounds **I** and **II**.

also present in the spectrum of the compound **II**. The spectrum of ^{1}H NMR revealed that the chemical shifts of the peaks at 2.74 and 3.70 ppm of compound **II** were kept in the same order comparing with the spectrum of the compound **I**, particularly because their chemical circumstances were not changed. From the chemical shifts and the peak area integrations of six peaks, the peaks representing protons on the chain of compound **II** were easily recognized. The spectra of IR and ^{1}H NMR of compounds **I** and **II** showed that the hydroxyl protection product and alkylation product possessed the structures as we desired.

In addition, compounds **I** and **II** were also subjected to liquid chromatography–mass spectrometer analyses with ESI. The spectra of compounds **I** and **II** were shown in Figures 4 and 5. In mass spectra using ESI, molecular ion peaks of compounds **I** and **II** were seen. The base peaks at *m/z* 250.1648 and 290.1956 could be assigned to $[M + H]^+$ (100%) molecular ion peaks of compounds **I** and **II**. As a result,

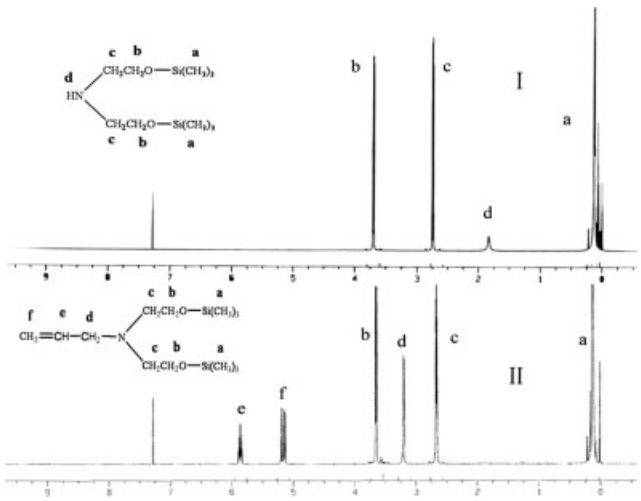


Figure 3 ^{1}H NMR spectra of compounds **I** and **II**.

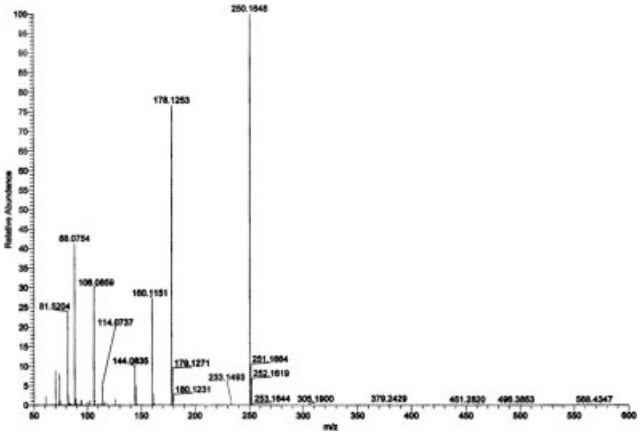


Figure 4 LC-MS spectrum of compound **I**.

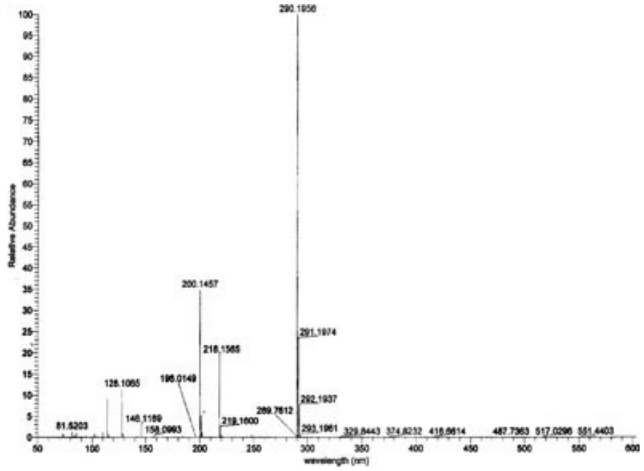
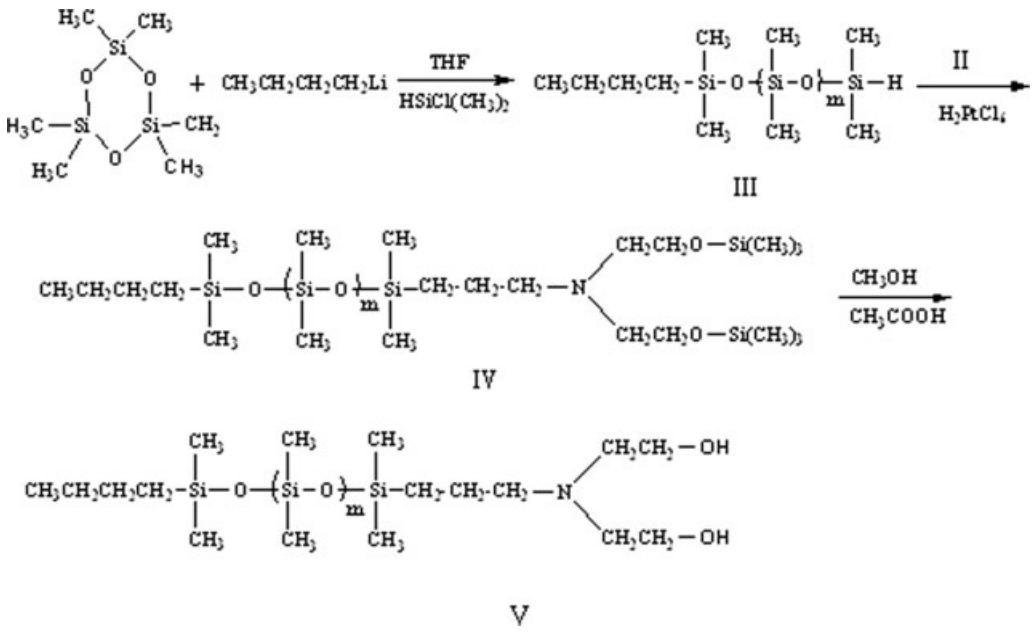


Figure 5 LC-MS spectrum of compound **II**.

molecular weight of compounds **I** and **II** were determined to be 249 and 289, well consistent with expected values, and their elemental compositions were $C_{10}H_{27}O_2Si_2N$ and $C_{13}H_{31}O_2Si_2N$.

Syntheses and characterization of compounds III, IV, and V

Compounds **III**, **IV**, and **V** were synthesized through anionic ring-opening polymerization, hydrosilylation, and deprotection as outlined in Scheme 3. Since the Si—H group can undergo the hydrosilylation reaction to add to unsaturated allyl compounds, H-containing silicone oil (**III**) was synthesized via anionic ring-opening polymerization so that it could react with the compound **II** prepared earlier. Hexamethylcyclotrisiloxane is known to polymerize with lithium initiators such as butyllithium.[12] Dimethylchlorosilane as end-capping agent was added to the reaction mixture to terminate the polymerization, and H-containing silicone oil was obtained. The reaction product was subjected to IR and ^{1}H NMR analyses (Fig. 6 and Fig. 7). The main characteristic of IR spectrum of H-containing silicone oil was that a strong Si—H vibration appeared at 2128 cm^{-1}. ^{1}H NMR spectrum also revealed that the peak at 4.63 ppm was assigned to Si—H. The molecular weight of H-containing silicone oil was determined by ^{1}H NMR, GPC, and titration (Table I). Then the hydrosilylation reaction happened between H-containing silicone oil and compound **II**. Comparing with the spectra of compound **II** and H-containing silicone oil, the hydrosilylation product **IV** mainly



Scheme 3 Syntheses of compounds **III**, **IV**, and **V**.

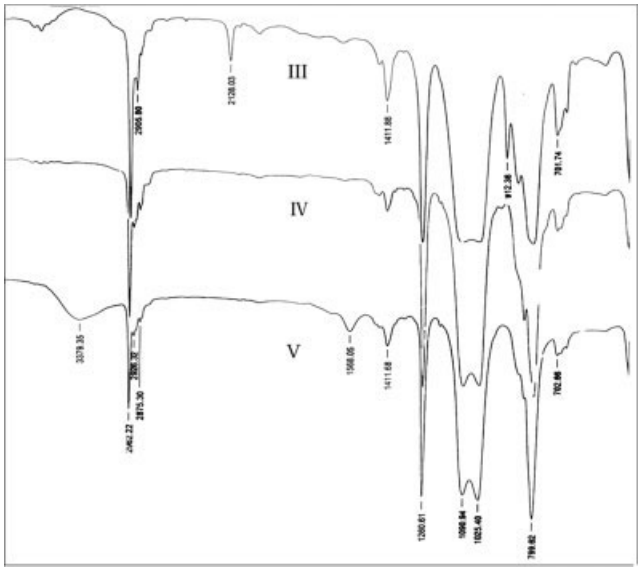


Figure 6 IR spectra of compounds **III**, **IV**, and **V**.

represented the following characteristics: Complete disappearance of C=C double bond vibration at 1642 cm^{-1} and Si—H vibration at 2128 cm^{-1}. This indicated that hydrosilylation reaction had happened between C=C double bond and Si—H. Meanwhile the data of ^{1}H NMR spectrum of hydrosilylation product **IV** including chemical shifts and peak area integrations also validated the occurrence of hydrosilylation reaction.

To create hydroxyl groups in the molecule, the hydrosilylation product **IV** was deprotected so that it became reactive towards isocyanate group in a subsequent step to prepare siloxane modified polyurethane. Because the Si—O—C bond was not stable in the presence of base or acid and easy to rupture, excessive methanol was added into the hydrosilylation product **IV** in the presence of acetic acid as catalyst to produce hydroxyl groups. In this step, it is possible that the tertiary amine would change into an ammonium, but when the reaction was over, the catalyst, acetic acid, must be neutralized. In this step, the ammonium was turned into the tertiary amine when the potassium hydroxide methanol solution was added into the resulting mixture. At last the substances with low boiling point in the resulting mixture were removed by vacuum to obtain the purer deprotection product. Comparing with ^{1}H NMR spectrum of hydrosilylation product, the deprotection product displayed that the peak at

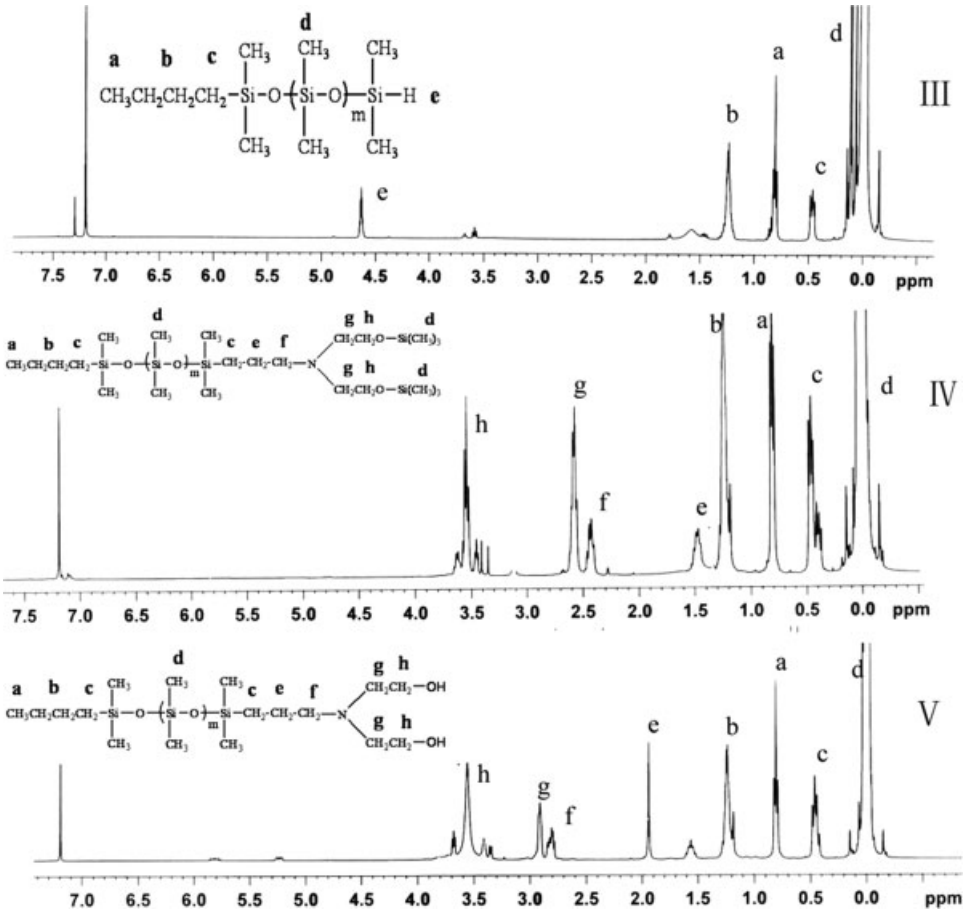


Figure 7 ^{1}H NMR spectra of compounds **III**, **IV**, and **V**.

TABLE I
Molecular Weight of H-Containing Silicone Oil

M_n by Theor.	M_n by Si—H	M_n by ^{1}H NMR	M_n by GPC	M_w by GPC	$\frac{M_w}{M_n}$
1000	1142	982	1788	2125	1.19

δ = 1.96 ppm was assigned to the hydroxyl proton in its ^{1}H NMR spectrum. Other chemical shifts of proton showed only limited variations because the chemical surroundings of these protons only slightly changed. This was reconfirmed by IR spectrum in which there was a hydroxyl vibration peak at 3379 cm^{-1}.

CONCLUSIONS

α-Butyl-ω-*N*,*N*-dihydroxyethylaminopropylpolydimethylsiloxane, a monotelechelic polydimethyl-siloxane with a diol end group which can modify other organic polymers by graft copolymerization, can be prepared by hydroxyl protection, alkylation, anionic ring-opening polymerization, hydrosilylation, and deprotection. The successful synthesis of this kind of compound is a matter of primary importance for researches on graft copolymerization.

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