Synthesis and characterization of α-butyl-ω-[3-[(2,2-dihydroxymethyl)-propionyloxy]]propyl polydimethyl siloxane

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Abstract: A novel polydimethylsiloxane containing two primary hydroxyl groups at one single chain end was synthesized by five-step reactions which included esterification, hydroxyl protection, anionic ring-opening polymerization, hydrosilylation and deprotection. The prepared compounds in each step were characterized. The results showed that at each step synthesis was successfully carried out and objective products could be achieved.

Introduction

Polydimethylsiloxanes (PDMS) containing hydroxyalkyl groups are a special type of functional silicone polymer. Owing to the intrinsic attributes of hydroxyalkyl groups, much attention has been attracted on the introduction PDMS into the chains of polyurethanes (PU) by the reaction between hydroxy groups and isocyanato groups to improve the performance of PU and expect to afford other specific characteristics inherent in PDMS materials such as heat resistance, surface properties, water repellency, biocompatibility, gas permeability etc [1].

For synthesis of PU-PDMS copolymers, block and graft copolymerization are two effective methods. One is by insertion of PDMS segments into PU chain to form block copolymers. The other is by attaching PDMS as the side chain of PU to form graft copolymers. The former has attracted much attention [2-5]. However, works concerning the latter were relatively scarce. That might be due to the reason that it is not easy to synthesize PDMS with a diol group at one single chain end.

Hisao et al. [6] synthesized 1-(2-hydroxymethyl-3-hydroxypropyl)-1,1,3,3,3-pentamethyldisiloxane via hydrosilylation reaction between 1,1,3,3,3-pentamethyldisiloxane and 2-methylene-1,3-propanediol (MPD). As far as we know, it is difficult to obtain MPD, because MPD was synthesized at 500 degrees centigrade. Hideki et al. [7] synthesized a series of uniform-size PDMS containing 3-[(2,3-dihydroxy)propoxy]propyl group at one single chain end. The compound has two hydroxyl groups at one single chain end, of which one is a primary hydroxyl group,
the other is a secondary hydroxyl group, but these two hydroxyl groups have different reactivities from each other.

In this paper, with the purpose to prepare PDMS with a diol group having same reactivities, a new route was designed for the synthesis of PDMS with two primary hydroxyl groups at one single chain end. All the resulting products in each step of synthesis were characterized.

**Results and discussion**

*Synthesis and characterization of compound I*

The compound I was prepared via esterification reaction between 2,2-bis(hydroxymethyl)propionic acid (DMPA) and allyl bromide (AB) (Scheme 1). There are two advantages in selecting allyl bromide rather than allyl alcohol as the reacting material. In general, esterification of carboxylic acids with alcohols to give esters is a typical reversible reaction in which the products and reactants are in equilibrium. The equilibrium may be influenced by either removing one product from the reaction mixture (for example, removal of the water by azeotropic distillation or absorption by molecular sieves) or by employing an excess of one reactant.

On the contrary, the reaction of an alkali carboxylate and an electrophilic alkylating agent such as an alkyl halide is not a reversible reaction and therefore can run to completion naturally. On the other hand, a few side reactions could be avoided. For
example, DMPA not only reacts with allyl alcohol in the presence of an acid catalyst, but also it can react with itself at the same condition.

The structure of I was first studied by FT-IR analysis, the corresponding spectra is shown in Fig.1. The FT-IR spectrum of I presents the characteristic absorption of both precursors. A strong absorption band associated to OH group was evidently observed at 3411 cm\(^{-1}\). The \(\nu_{c=c}\) and \(\nu_{c=o}\) bands are also observed at 1653 cm\(^{-1}\) and 1724 cm\(^{-1}\), respectively. In addition, a new band associated to C-O-C group was observed at 1042 cm\(^{-1}\). The FT-IR analysis indicates that AB reacted with potassium salt of DMPA and I could be synthesized. In order to confirm the formation of I better, I was then subjected to \(^1H\) NMR analysis (Fig.2). From the chemical shifts and the peak area integrations, the peaks representing protons labelled from 1 to 6 are easily assigned. This result is in agreement with that obtained by FT-IR analysis, and I is synthesized successfully as expected.

**Fig. 2.** \(^1H\) NMR spectra of I.

**Synthesis and characterization of compound II**

As we know, hydroxyl groups could react with Si-H bonds to release hydrogen gas, and the dehydrogenation reaction could reduce the yield of final compound. To prevent the dehydrogenation reaction happening, the protection is essential. The hydroxyl protection is depicted in Scheme 2.

As in compound I, compound II was first subjected to IR analysis. In comparison with the spectra of I, the spectrum of compound II (Fig. 3) exhibits the following characteristics: a) Complete disappearance of OH vibration peak, which was observed in I spectrum at 3411 cm\(^{-1}\), b) appearance of Si-CH\(_3\) vibration and Si-O-C vibration peak at 1252 cm\(^{-1}\) and 1088 cm\(^{-1}\), these peaks were absent in I spectrum, c) other peaks, i.e. C=C double bond vibration at 1650 cm\(^{-1}\), C=O double bond vibration at 1735 cm\(^{-1}\) are also observed. It was indicated that the new trimethylsilyl groups formed accompany with the disappearance of hydroxyl groups. In another word, the
two hydroxyl groups were protected successfully. The $^1$H NMR analysis result also confirms the conclusion. The $^1$H NMR spectrum of II (Fig. 4) shows that the peak at $\delta$=3.07 ppm assigned to the hydroxyl proton disappeared, and that a new peak assigned to the Si-CH$_3$ proton is observed at $\delta$=-0.10 ppm.

\[
\text{I} + (\text{CH}_3)_3\text{SiNHSi(\text{CH}_3)_3} \rightarrow \text{CH}_2=\text{CHCH}_2\text{OOCCH}_3 + \text{NH}_3
\]

\[
\text{CH}_2\text{OSi(\text{CH}_3)_3}
\]

\[
\text{II}
\]

**Scheme 2.** Synthesis of II.

**Fig. 3.** FT-IR spectra of II.

**Fig. 4.** $^1$H NMR spectra of II.
Synthesis and characterization of compound III, IV and V

The compound III, IV and V were synthesized by anionic ring-opening polymerization, hydrosilylation and deprotection, respectively. The synthesis route of them is depicted by Scheme 3.

Scheme 3. Synthesis of III, IV and V.

Due to the ring-strain of D₃, which enhances the reactivity of the Si-O bonds, D₃ can be polymerized in a living character in the presence of alkyl-lithium initiators and low concentrations of a polar solvent to produce polymers with narrow molecular weight distributions. The compound III was obtained after termination reaction of the living PDMS with DMCS. Three parallel equilibrium reactions were conducted with varying the ratio of D₃/initiator in order to achieve PDMS with different segment length consisting of dimethylsiloxane units. The main characteristics of FT-IR spectrum of III (Fig. 5) is that a strong Si-H vibration peak appears at 2128 cm⁻¹. ¹H NMR spectrum (Fig. 6) also reveals that the peak assigned to Si-H proton appears at δ=4.63 ppm.

The compound IV was prepared by hydrosilylation reaction of II with III in presence of H₂PtCl₆. In comparison with the FT-IR spectra of II and III, the spectrum of IV (Fig.5) exhibits the following characteristics: a) complete disappearance of C=O double bond vibration, which was observed in spectrum of II at 1650 cm⁻¹, b) complete disappearance of Si-H vibration, which was observed in spectrum of III at 2128 cm⁻¹, c) appearance of C=O double bond vibration at 1735 cm⁻¹. According to these changes, the formation of IV through the hydrosilylation reaction is confirmed.

After hydrosilylation reaction, the protective groups should be removed in order to create two hydroxyl groups in the molecule, so that it became reactive towards...
isocyanate group in a subsequent step to prepare siloxanes modified polyurethane. Si-O-C bond is not stable in water or alcohol medium and easy to hydrolyze or alcoholize in the presence of weak acid. Excessive methanol was mixed with IV in the presence of acetic acid to produce hydroxyl groups. From the spectrum of V (Fig. 5), the hydroxyl vibration peak is observed at 3445 cm⁻¹. The ¹H NMR spectrum of V is shown in Fig. 7. The peaks representing protons labelled from 1 to 8 are assigned from the chemical shifts and the peak area integrations.

**Fig. 5.** FT-IR spectra of III, IV and V.
Based on the proton peak integration, the molecular weight of III (Table 1) and V (Table 2) were estimated along with that obtained via GPC, functional group analysis (based on Si-H group or OH group) as well as the theoretical value. It is noteworthy that the theoretical molecular weight of III and V are in good agreement with the values measured from chemical titration or $^1$H NMR. However, the value from GPC is slightly larger than the theoretical value. This might be due to the fact that the polystyrene was used as the polymer standard in these tests, which may lead to inaccurate result knowing that these two polymers were of very different natures.

**Fig. 6.** $^1$H NMR spectra of III.

**Fig. 7.** $^1$H NMR spectra of V.
Tab. 1. Molecular weight of III.

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Tab. 2. Molecular weight of compound V.

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Conclusions

Polydimethylsiloxanes containing two primary hydroxyl groups at only one of the chain ends were synthesized successfully by five-step reactions which included esterification, hydroxyl protection, anionic ring-opening polymerization, hydrosilylation and deprotection. The outcome of each step was characterized by FT-IR and <sup>1</sup>H NMR, and the analysis result indicated that at each step synthesis was carried out successfully as expected. The final products are useful for the preparation of the polycondensation polymers having pendant polysiloxane chains, especially to prepare PU-PDMS graft copolymers in the future.

Experimental part

Materials and methods

2,2-Bis(hydroxymethyl)propionic acid (DMPA), hexamethyldisilazane (HMDA) and allyl bromide (AB) were all industrial grade and were purchased from Huzhou Changsheng Chemicals Co. Ltd., Shanghai Huitian New Chemical Material and Zouping Mingxing Chemicals, respectively. Benzene (Shanghai General Factory of Chemicals) and tetrahydrofuran (THF, Tianjin Dahua Chemicals) were A.R. and were refluxed over sodium/potassium alloy. Dimethylformamide (DMF, Chemical Engineering Institute of Shandong) and methanol (Tianjin Dahua Chemicals), Dimethylichlorosilane (DMCS, Datian Chemical Auxiliaries Research Institute) and hexamethylocyclotrisiloxane (D<sub>3</sub>, APCR, Karlsruhe, FRG) were all A.R. and were used as received without further treatment. n-Butyllithium (Shanghai Shanglunhuayu Chemical Co. Ltd.) was used after titration.

Samples were cross-examined using different instruments combined with chemical analysis method. The Si-H amount in polydimethylsiloxane with Si-H group at one end and hydroxyl group content in α-butyl-ω-[3-{(2,2-dihydroxyethyl)-propionyloxy}]propyldimethylsiloxane were estimated by chemical titration, of which the details are available elsewhere [8-9]. Fourier transform infrared spectra were recorded on a Nicolet 470 FT-IR Spectrometer. <sup>1</sup>H NMR spectra were recorded at 27 °C on Bruker AVANCE 600 with CD<sub>3</sub>Cl as solvent and tetramethylsilane (TMS, δ= 0 ppm) as internal standard. Liquid chromatography mass spectrometer analyses were carried out in a 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. GPC was performed in a Waters 1525 Binary HPLC Pump using Waters 2414 Refractive Index Detector, Styragel HT 2, 3, 4 as columns, and THF as eluant.

**Synthetic procedures**

-Synthesis of (2,2-dihydroxymethyl)propionyloxy, 2-propenyl ester (I)

13.37 g DMPA, 7.00 g potassium carbonate anhydrous and 100 mL DMF were added sequentially into the flask. The resulting solution was heated to 40 °C and 14.42 g AB was added drop wise. The reaction mixture was then slowly heated to 65 °C and kept at this temperature for 6 h. After filtration, I was separated through distillation under reduced pressure (1.33 KPa) from the crude products. The distillate between 148 and 150 °C was collected and 15.22 g colourless liquid was obtained with a yield of 88%. FT-IR (KBr, ν, cm⁻¹): 1663 (C=O), 1042 (C-O-C), 1724 (C=O), 3411 (OH). ¹H NMR (CDCl₃, 600MHz, δppm): 5.30 (2H, q, CH₂=CH), 5.85 (1H, m, CH=CH₂), 4.60 (2H, m, CH-CH₂-O), 3.64 and 3.83 (4H, q, C-CH₂-OH), 3.07 (2H, s, CH₂-OH), 1.03 (3H, s, CH₃-C). HRMS (ESI, 70eV): m/z (%) =175.2175 (100) [M+H]+, calcd for C₉H₁₄O₄.

-Synthesis of [2,2-bis(trimethylsilyloxy)methyl]propionyloxy, 2-propenyl ester (II)

10.03 g I was located into a 100 mL round-bottomed flask, and then 14.25 g HMDA was added dropwise into the flask under agitation at room temperature. This mixture solution was heated to 90 °C and kept at this temperature for 8 h. The distillate between 250 and 252 °C was collected and 15.34 g pale yellow liquid (II) was obtained with a yield of 84%. FT-IR (KBr, ν, cm⁻¹): 1650 (C=C), 1735 (C=O), 1252 (Si-CH₃), 1088 (Si-O-C). ¹H NMR (CDCl₃, 600 MHz, δppm): 5.26 (2H, q, CH₂=CH), 5.81 (1H, m, CH=CH₂), 4.50 (2H, m, CH-CH₂-O), 3.60 (4H, q, CH₂-OSi(CH₃)₃), 1.05 (3H, s, CH₃-C), -0.10 (18H, s, CH₂-O(CH₃)₃). HRMS (ESI, 70eV): m/z (%) = 319.6425 (100) [M+H]+, calcd for C₁₄H₃₀O₄Si₂.

-Synthesis of polydimethylsiloxanes with Si-H group at one end (III)

According to reported procedures [10-11], III was prepared by the anionic ring-opening polymerization of D₃ using n-butyllithium as initiator and using DMCS as terminating agent in a mixed solvent of benzene and THF. After removal of solvent and LiCl precipitate, colourless transparent liquid was obtained with a yield of 88%. FT-IR (KBr, ν, cm⁻¹): 2128 (Si=O), 1733 (C=O), 1261 (Si-CH₃), 1090 (Si-O-Si). ¹H NMR (CDCl₃, 600 MHz, δppm): 0.00 (122H, s, Si-CH₃), 0.46 (2H, t, Si-CH₂), 0.80 (3H, t, CH₃-CH₂), 1.24 (4H, m, CH₂-CH₂-CH₃), 4.62 (1H, s, Si-H).

-Synthesis of α-butyl-ω-(3-[2,2-bis(trimethylsilyloxy)methyl]propionyloxy)propylpolydimethylsiloxanes (IV)

A four neck flask, equipped with a stirrer, a thermometer, a nitrogen purge, and a reflux condenser (equipped with a tubular dryer filled with anhydrous calcium chloride), was charged with 6.78g II, 15 mL toluene and 0.10 g chloroplatinic acid solution (2% in isopropanol). The flask was heated to 90 °C, followed by dropwise addition of 26.65 g III, and kept at this temperature for 8 h. Toluene and excessive III were removed under vacuum. 28.65 g bright yellow liquid (IV) was obtained with a yield of 89%. FT-IR (KBr, ν, cm⁻¹): 1735 (C=O), 1261 (Si-CH₃), 1093 (Si-O-Si). ¹H NMR (CDCl₃, 600 MHz, δppm): 0.00 (140H, s, Si-CH₃), 0.46 (4H, m, Si-CH₂), 0.81
(3H, t, CH₃-CH₂), 1.06 (3H, s, CH₃-C), 1.24 (4H, m, CH₂-CH₂-CH₃), 1.61 (2H, m, CH₂-CH₂-O), 3.59 (4H, m, CH₂-OSi(CH₃)₃), 3.95 (2H, m, CH₂-CH₂-O).

-Synthesis of α-butyl-ω-[3-[(2,2-dihydroxymethyl)propionyloxy]propylpolydimethylsiloxanes (V)

10.02 g IV and 100 g methanol were added into three necked flask equipped with thermometer, condenser and magnetic stirrer, followed by addition of 0.1 mL acetic acid as catalyst. The reaction mixture was stirred at reflux for 6 h. Acetic acid and excessive methanol were removed under vacuum. 8.59 g bright yellow liquid (V) was obtained with a yield of 93%. FT-IR (KBr, v, cm⁻¹): 1730 (C=O), 1261 (Si-CH₃), 1094 (Si-O-Si), 3445 (OH).

1H NMR(CDCl₃, 600MHz, δppm): 0.00 (12H, s, Si-CH₃), 0.46 (4H, m, Si-CH₂), 0.81 (3H, t, CH₃-CH₂), 1.05 (3H, s, CH₃-C), 1.25 (4H, m, CH₂-CH₂-CH₃), 1.62 (2H, m, CH₂-CH₂-O), 3.68 and 3.84 (4H, m, CH₂-OH), 4.04 (2H, m, CH₂-CH₂-O).

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References