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Synthesis and characterization of α-butyl-ω-{3-[(2,2-dihydroxymethyl)-propionyloxy]}propylpolydimethylsiloxanes

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Abstract

A series of polydimethylsiloxanes containing two primary hydroxyl groups at one single chain end were 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 each step synthesis was successfully carried out and objective products could be achieved.

Keywords: Esterification; Hydroxyl protection; Anionic ring-opening polymerization; Hydrosilylation; Deprotection; α-Butyl-ω-{3-[(2,2-dihydroxymethyl)propionyloxy]}propylpolydimethylsiloxane

Polydimethylsiloxanes (PDMS) possess flexible molecular structures and exhibit considerably different and unique 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 and biocompatibility [1]. Therefore, it is of great interest to design copolymers composed of common organic polymers and PDMS to develop unique properties of the resulting copolymers.

For synthesis of PDMS-containing copolymers, block and graft copolymerization are two effective methods, one is by insertion of PDMS segments into organic polymers chain to form block copolymers [2–5], the other is by attaching PDMS as the side chain of the organic polymers to form graft copolymers [6]. The former has attracted much attention. However, works concerning the latter were relatively scarce, and particularly the studies about polydimethylsiloxane–polyurethane graft copolymers were rare. The reason could be attributed to the difficulty of synthesizing PDMS with a diol group at one single chain end.

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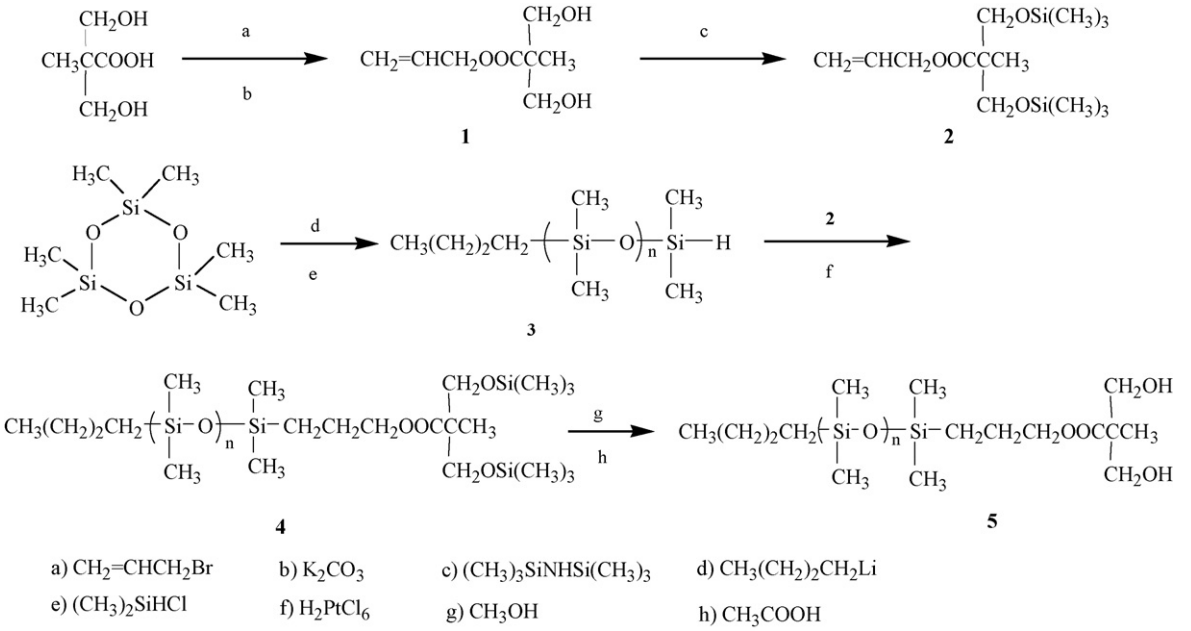

Scheme 1. Synthesis of PDMS containing two primary hydroxyl groups at one single chain end.

In this paper, a new route (Scheme 1) was designed for the synthesis of PDMS with two primary hydroxyl groups at one single chain end. All the resulting products in each step synthesis were characterized.

1. Experimental

Dimethylolpropionic 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), dimethylchlorosilane (DMCS, Datian Chemical Auxiliaries Research Institute) and hexamethylcyclotrisiloxane (D_3, ABCR, 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 was estimated by chemical titration, of which the details are available elsewhere [7]. Fourier transformed infrared spectra were recorded on a Nicolet 470 FT-IR Spectrometer. ^{1}H NMR spectra were recorded at 27 °C on Bruker AVANCE 600 with CD_3Cl as solvent and tetramethylsilane (TMS, $\delta = 0$ ppm) as internal standard. Liquid chromatography mass spectrometer analyses were carried out onnLTQ 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 with Waters 1525 Binary HPLC Pump using Waters 2414 Refractive Index Detector, Styragel HT 2, 3, 4 as columns, and THF as eluant.

1.1. Synthesis of (2,2-dihydroxymethyl)propionyloxy, 2-propenyl ester ***1***

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 dropwise. The reaction mixture was then slowly heated to 65 °C and kept at this temperature for 6 h. After filtrating, **1** 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

Table 1
Molecular weight of **3**.

M_n by theory	M_n by Si–H	M_n by ^{1}H NMR	M_n by GPC	PDI
1500	1460	1522	2003	1.17

colorless liquid was obtained with a yield of 88%. FT-IR (KBr, ν, cm^{-1}): 1663 (C=C), 1042 (C–O–C), 1724 (C=O), 3411 (OH). ^{1}H NMR ($CDCl_3$, 600 MHz, δ ppm): 5.30 (q, 2H, CH_2=CH), 5.85 (m, 1H, CH=CH_2), 4.60 (m, 2H, CH–CH_2–O), 3.64 and 3.83 (q, 4H, C–CH_2–OH), 3.07 (s, 2H, CH_2–OH), 1.03 (s, 3H, CH_3–C). MS (ESI, 70 eV): *m/z* (%) = 175.2175 (100) $[M + H]^+$, $C_8H_{14}O_4$.

1.2. Synthesis of [2,2-bis(trimethylsilyloxymethyl)]propionyloxy, 2-propenyl ester ***2***

10.03 g **1** was located into a 100 mL round-bottomed flask, and then 14.25 g HMDA was dropwise added 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 (**2**) was obtained with a yield of 84%. FT-IR (KBr, ν, cm^{-1}): 1650 (C=C), 1735 (C=O), 1252 (Si–CH_3), 1088 (Si–O–C). ^{1}H NMR ($CDCl_3$, 600 MHz, δ ppm): 5.26 (q, 2H, CH_2=CH), 5.81 (m, 1H, CH=CH_2), 4.50 (m, 2H, CH–CH_2–O), 3.60 (q, 4H, CH_2–$OSi(CH_3)_3$), 1.05 (s, 3H, CH_3–C), −0.10 (s, 18H, CH_2–$OSi(CH_3)_3$). MS (ESI, 70 eV): *m/z* (%) = 319.6425 (100) $[M + H]^+$, $C_{14}H_{30}O_4Si_2$.

1.3. Synthesis of polydimethylsiloxanes with Si–H group at one end ***3***

According to reported procedures [8,9], **3** was prepared by the anionic ring-opening polymerization of D_3 using *n*-butyllithium as initiator and DMCS as terminating agent in a mixed solvent of benzene and THF. After removing of solvent and LiCl precipitate, colorless transparent liquid was obtained with a yield of 88%. Based on the proton peak integration, the molecular weight of **3** was estimated (Table 1) along with that obtained via GPC, functional group analysis (based on Si–H group) as well as the theoretical value. It is noteworthy that the theoretical molecular weight of **3** is 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 test, which may lead to inaccurate result knowing that these two polymers are of very different natures. FT-IR (KBr, ν, cm^{-1}): 2128 (Si–H), 1261 (Si–CH_3), 1090 (Si–O–Si). ^{1}H NMR ($CDCl_3$, 600 MHz, δ ppm): 0.00 (s, 122H, Si–CH_3), 0.46 (t, 2H, Si–CH_2), 0.80 (t, 3H, CH_3–CH_2), 1.24 (m, 4H, CH_2–CH_2–CH_3), 4.62 (s, 1H, Si–H).

1.4. Synthesis of α-butyl-ω-{3-[2,2-bis(trimethylsilyloxymethyl)]propionyloxy}propylpolydimethylsiloxanes ***4***

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 excessive **2**, 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 **3**, and kept at this temperature for 8 h. Toluene and excessive **2** were removed under vacuum. 28.65 g bright yellow liquid (**4**) was obtained with a yield of 89%. FT-IR (KBr, ν, cm^{-1}): 1735 (C=O), 1261 (Si–CH_3), 1093 (Si–O–Si). ^{1}H NMR ($CDCl_3$, 600 MHz, δ ppm): 0.00 (s, 140H, Si–CH_3), 0.46 (m, 4H, Si–CH_2), 0.81 (t, 3H, CH_3–CH_2), 1.06 (s, 3H, CH_3–C), 1.24 (m, 4H, CH_2–CH_2–CH_3), 1.61 (m, 2H, CH_2–CH_2–O), 3.59 (m, 4H, CH_2–$OSi(CH_3)_3$), 3.95 (m, 2H, CH_2–CH_2–O).

1.5. Synthesis of α-butyl-ω-{3-[(2,2-dihydroxymethyl)propionyloxy]}propylpolydimethylsiloxanes ***5***

10.02 g **4** and 100 g methanol were added into three-necked flask equipped with thermometer, condenser and magnetic stir, 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 (**5**) was obtained with a yield of 93%. Based on the proton peak integration, the molecular weight of **5** was estimated (Table 2) along with that obtained via GPC, functional group analysis (based on hydroxyl) as well as the theoretical value. FT-IR

Table 2
Molecular weight of **5**.

M_n by theory	M_n by –OH	M_n by ^{1}H NMR	M_n by GPC	PDI
1674	1798	1701	2238	1.18

(KBr, ν, cm^{-1}): 1730 (C=O), 1261 (Si–CH_3), 1094 (Si–O–Si), 3445 (OH). ^{1}H NMR($CDCl_3$, 600 MHz, δ ppm): 0.00 (s, 122H, Si–CH_3), 0.46 (m, 4H, Si–CH_2), 0.81 (t, 3H, CH_3–CH_2), 1.05 (s, 3H, CH_3–C), 1.25 (m, 4H, CH_2–CH_2–CH_3), 1.62 (m, 2H, CH_2–CH_2–O), 3.68 and 3.84 (m, 4H, CH_2–OH), 4.04 (m, 2H, CH_2–CH_2–O), 4.71 (s, 2H, OH).

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