

## Synthesis and characterization of $\alpha$ -butyl- $\omega$ -{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.

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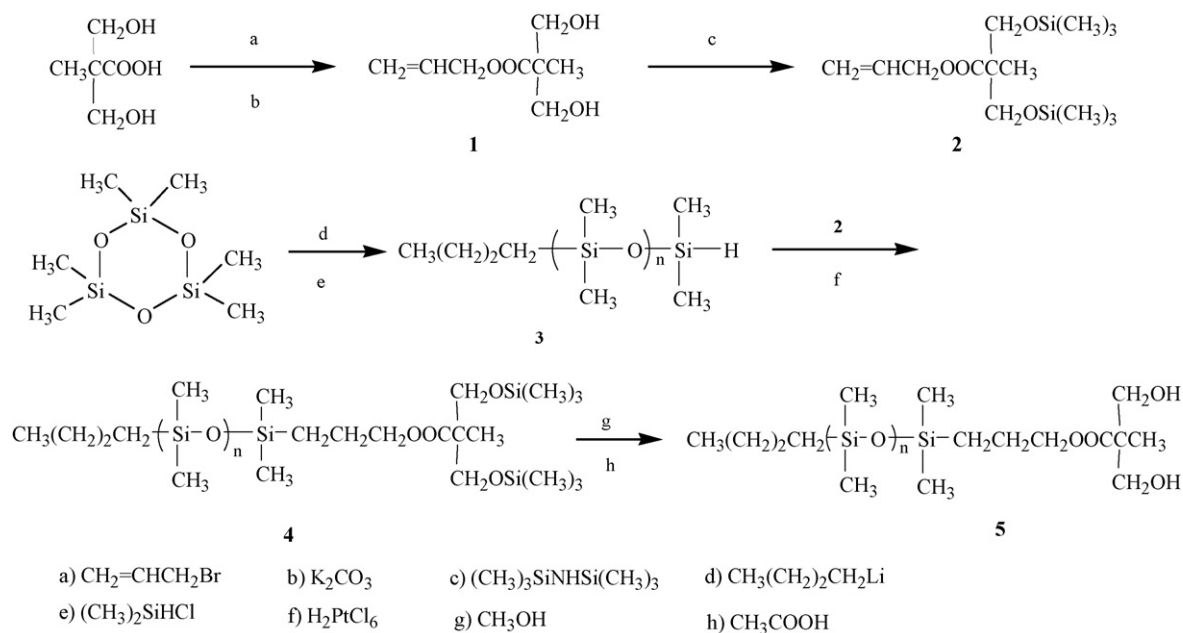
**Keywords:** Esterification; Hydroxyl protection; Anionic ring-opening polymerization; Hydrosilylation; Deprotection;  $\alpha$ -Butyl- $\omega$ -{3-[(2,2-dihydroxymethyl)propionyloxy]}propylpolydimethylsiloxane

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 (HMDS) 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<sub>3</sub>, 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. <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 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

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