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Synthesis, characterization and physicochemical properties of glycosyl-modified polysiloxane

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ABSTRACT

Four glycosyl-modified polysiloxane (GPSO) biosurfactants were designed and synthesized via two-step reactions using green materials. The physicochemical properties: surface activity and aggregation behaviors in aqueous solution were systematically investigated. Investigation of the surface tension indicates that GPSO have relatively low critical aggregation concentrations (CAC) and surface tensions at CAC (γ_{CAC}) compared with hydrocarbon surfactant. Adsorption at the air-water interface and the formation of micelles in aqueous are spontaneity and the tendencies of adsorption are favored over the process of micellization. Dynamic surface tension results indicate that D-glucoheptono-1, 4-lactone modified polysiloxanes (GHL@Si) have good diffusion ability than that of glucono-δ-lactone modified polysiloxanes (GL@Si). Transmission electron microscopy (TEM) and Dynamic light scattering (DLS) results indicate that part of biosurfactants can form spherical aggregates.

1. Introduction

Compared with the carbon chain polymers, polymers with polysiloxane chain possess remarkable properties such as flexibility, low surface energy, biocompatibility and low toxicity, which can be used as bio-materials raw material. Modified polysiloxanes polymers are widely used in the fields of coating, adhesives, impact-resistance plastic, etc. [1, 2]. Amphiphilic polysiloxane surfactants, as a kind of modified polysiloxanes polymers, have been used as emulsifiers and spreading agents, wetting agents, anti-foaming agents and agricultural adjuvant due to its good emulsifying wettability properties and surface activity both in aqueous and organic solvent [3, 4].

Compared with conventional carbon chain surfactants, surfactants structured with polysiloxanes chains, are effective in reducing the surface tension in both aqueous and nonaqueous media due to a lower intermolecular cohesive force and the greater flexibility of polysiloxanes chains [5–7]. And such surfactants have been extensively used as emulsifiers, spreading agents, wetting agents and antifoaming agents [8].

In the past few years, many kinds of polysiloxane surfactants have been synthesized by hydrosilylation reaction. Dae-won Chung synthesized series of polydimethylsiloxane grafted with polyethyleneoxide (PDMS-g-PEO) by two-step reactions and the surface properties of PDMS-g-PEO were investigated by comparing the each effect caused by EO content [9]. M.M.A. EL-Sukkary successfully synthesized three series of amino-grafted polysiloxane surfactants. And their surface activities, aggregation behavior in aqueous solution, interfacial tension, foaming power, emulsification power, surface parameters, micellization and adsorption in liquid/air interfaces thermodynamics have been investigated [10]. Polysiloxane grafted polyamide-amine surfactants also have been prepared by grafting the single epoxy terminated polydimethylsiloxane onto the dendritic polyamide-amine. Furthermore, the stability, surface activity and emulsifying ability of polysiloxane grafted polyamide-amine surfactants were studied [11]. Polyglycerol modified polysiloxane surfactants [12] and butynediol-ethoxylate modified polysiloxanes [13, 14] have also been synthesized and their physicochemical properties have been studied systematically.

With the increase of surfactants usage and deterioration the ecosystem, green and environmental friendly surfactants which are made of natural renewable materials, have aroused the world's attention and become succedaneums of conventional surfactants in the last decade [15]. Green surfactants structured with carbon chains, such as alkyl polyglycoside (APG), have been widely used in detergent, cosmetics, and agriculture surfactants [16]. As a kind of green biologic carbohydrate material, lactones (such as glucono-δ-lactone) can be used to prepare carbohydrate-based surfactants. However, researches and application polysiloxanes surfactants made from renewable raw material are relatively scarce [17, 18].

In this work, green biologic ingredients glucono-δ-lactone (GL) and D-glucoheptono-1,4-lactone (GHL) were used to synthesize glycosyl-modified polysiloxanes green biosurfactants. The structures of biosurfactants were confirmed by FT-IR, ^{1}HNMR, ^{29}Si NMR and GPC. The effects of structure of biosurfactants on the surface properties and

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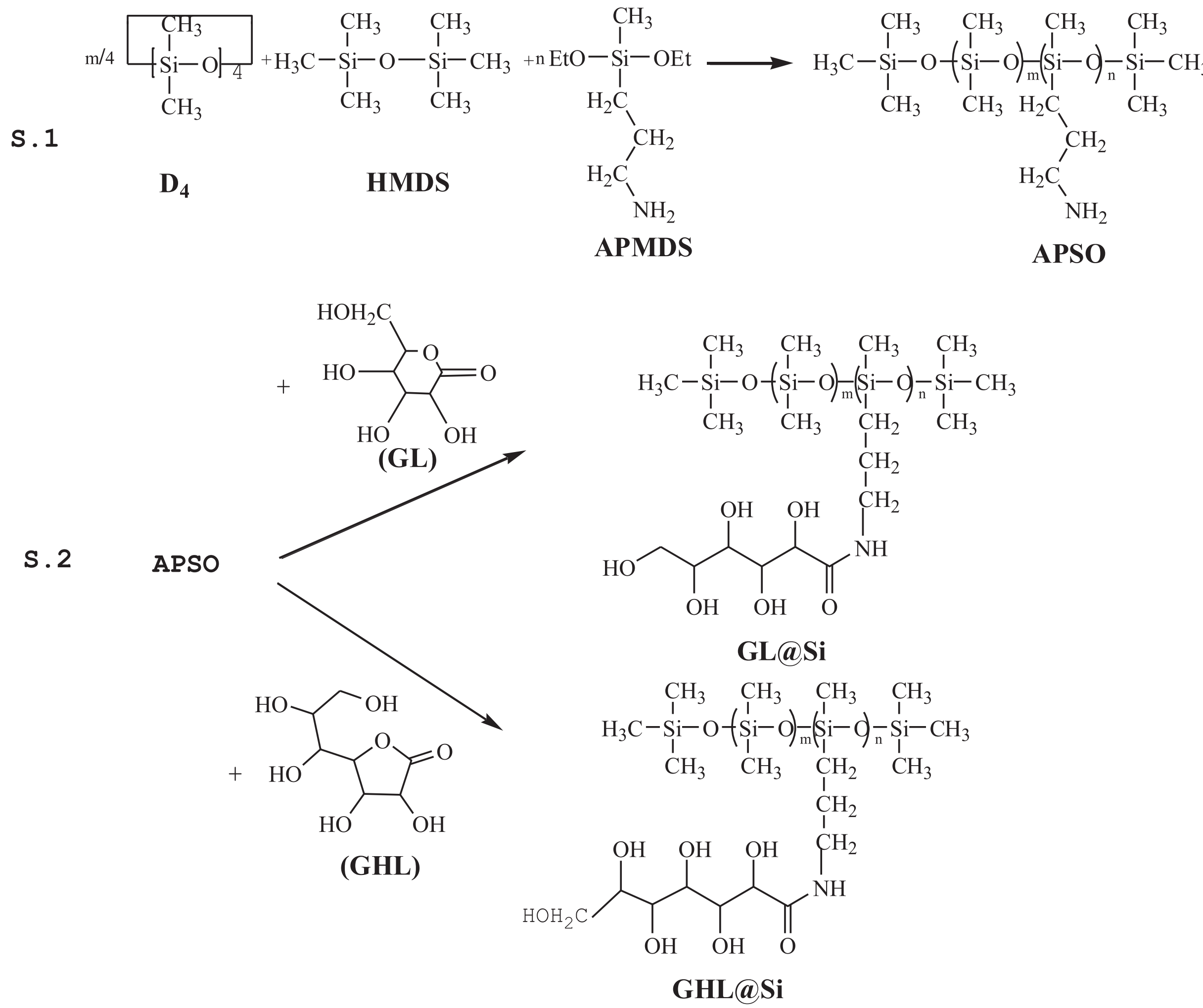

Fig. 1. Synthetic route of GPSO.

aggregation behavior in aqueous solution were investigated by means of surface tension measurements, dynamic light scattering (DLS) and transmission electron microscopy (TEM).

2. Materials and methods

2.1. Materials

Octamethylcyclotetrasiloxane (D_4) was purchased from Shenzhen Osbang New Material Co. Ltd. (China), 3-aminopropyl-methyl-diethoxysilane (APMDS) was obtained from Shanghai Molbase Biotechnology Co. Ltd. (China). Hexamethyldisiloxane (HMDS) was obtained from Hangzhou Guibao Chemical Co. Ltd. (China), Tetramethylammonium hydroxide (TMAH) and glucono-δ-lactone (GL) was purchased from Aladdin (China), D-glucoheptono-1, 4-lactone (GHL) was obtained from Sigma-Aldric. D_4 and APMDS were purified by reduced pressure distillation before used, and other chemical reagents were used as received.

2.2. Synthesis of GPSO

The synthesis procedure of GPSO involves two steps. Initially the intermediate aminopropyl polysiloxanes (APSO) is formed by polymerization of D_4 with APMDS and HMDS as shown in Fig. 1 (S. 1). The reaction effective concentration of catalyzer TMAH was 1%. TMAH was used in the form of tetramethylammonium hydroxide silicate salt (1%), which was carried out at 80 °C by D_4 and under a pressure reducing condition. The reactions mixture of APSO, APMDS, D_4 and catalyzer was stirred for 9 h at 90 °C under nitrogen atmosphere. The catalyzer was inactivated at 140 °C after polymerization. The purification of APSO was performed at 160 °C under a pressure reducing condition to eliminate unreacted materials and low weight oligomers. Two APSO products (APSO-1 and APSO-2) with different feeding ratio (listed in Table 1) were obtained.

APSO was then reacted with lactone (GL or GHL) using methanol as solvent at refluxes temperature for 12 h as shown in Fig. 1 (S. 2). The reactants were taken out in a 1:1 M ratio (lactone and amine content). Four GPSO were obtained after distillation and evaporation of the solvent: GL modified APSO-1 (GL@Si-1), GHL modified

Table 1
Effect of the feeding ratio of n (D4): n (APMDS) on the structure of APSO.

APSO	Feed ratio D_4: APMDS	M_n (expected)	GPC result		Amine content (mmol/g)	
			M_n	M_w	Expected	Actual
APSO-1	1:2	628	851	886	2.89	3.76
APSO-2	1:4	862	936	1074	4.32	5.06