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Polyglycerol modified polysiloxane surfactants: Their adsorption and aggregation behavior in aqueous solution

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ABSTRACT

A simple process to synthesize polyglycerol modified polysiloxane surfactants has been carried out applying a “grafting-to” approach. After formation of allyl polyglycerol ether (APGE) from diglycerol (DGY) and allyl glycidyl ether (AGE), polysiloxane modified by designed number of polyglycerol groups (PHMS-APGE) were obtained by connecting the APGE structure to different Si–H functionalized polyhydromethyl siloxane (PHMS). The synthesized APGE-PHMS were characterized by IR and ¹H NMR. Solubility measurements showed that the solubility of the as-prepared polymers increased in polar solvents with the increasing of the amount of hydrophilic APGE groups. Furthermore, the surface activity, surface adsorption, aggregation and spreading behaviors of APGE-PHMS were investigated utilizing surface tension measurements, dynamic light scattering (DLS), transmission electron microscopy (TEM) and contact angle measurements. The results showed that critical aggregation concentration (CAC) and the time needed to reach adsorption equilibrium on water surface decrease systematically with the increase in the number of APGE groups. These polymers in aqueous solutions could aggregate to form spherical assemblies. Moreover, the spreading behavior of these polymers on low energy surface was found to be influenced by the number of hydrophilic APGE groups.

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Introduction

Silicones have drawn people's attention for many years due to their unique properties. For instance they exhibit constant viscosity over a broad temperature range as well as an extremely high gas permeability and absolutely bio-inert. Thus, silicones are widely used in cosmetics, medicine, coatings, electronics and textiles, and so on [1]. Nevertheless, the hydrophobicity, which is the most significant feature of silicone, has always been a drawback for a great number of applications [2,3]. Therefore, current attempts mostly focus on combination of silicones and hydrophilic materials in order to combine the unique silicone-specific properties with hydrophilicity. Jonas and Stadler focused

on the attachment of various kinds of oligo- and polysaccharides [4–6]. Böhm et al. synthesized hydrophilic silicone with glycerol side chains [2]. Further information on polymers combining silicone with various other hydrophilic groups, either in the form of random or block copolymers or with grafted [7], branched [8–10], star-shaped [11], or cross-linked [12–14] polymers, has been reported. Polyether modified polysiloxane is one of the most popular hydrophilic silicones. The specific properties of polyether modified polysiloxane have also been studied in a lot of publications [15,16]. However, the raw material of polyether may contain carcinogenic 1,4-dioxane, which is banned in some personal care products [17]. At the same time, the raw material for polyether, which depends on fossil fuels, is not sustainable.

Glycerol is water-soluble and renewable. Moreover, with the development of biodiesel, surplus glycerol has become an urgent issue. But little research has been done on combination of silicone and hydrophilic polyglycerol. Here we report a two-step synthetic approach to graft polyglycerol groups to the polysiloxane backbone. We further investigated their basic properties and application performances.

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Experimental

Materials

Diglycerol (DGY, 81%) and allyl glycidyl ether (AGE, 99%) were purchased from TCI. Potassium hydroxide (KOH, 99%) was supplied by Tianjin Chemical Reagent Co., Ltd. (China). Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9%) was provided by Nanjing Chemical Reagent Co., Ltd. (China). Isopropanol (IPA, 99.8%) and sulfuric acid (H_2SO_4 , 98%) were purchased from Beijing chemical Reagent Co., Ltd. (China). Other reagents, i.e., including octamethyl cyclotetrasiloxane (D_4), poly(methylhydrosiloxane) (Mw 3792) and hexamethyldisiloxane (MM) were of technical grade and obtained from Zhejiang Runhe Organosilicon New Material Co., Ltd. (China). Double distilled water was used for analyzes and property measurements. All commercially available chemicals were used as received without any further purification.

Synthesis of polyglycerol-modified polysiloxane (APGE-PHMS)

Synthesis of allyl polyglycerol ether (APGE) and polyhydromethyl siloxane (PHMS)

Under N_2 , 19.94 g (0.12 mol) of diglycerol was reacted with 11.42 g (0.10 mol) of allyl glycidyl ether in the presence of potassium hydroxide as catalyst and the mixture was stirred for 3 h at a reflux temperature of 90°C . Then the product was neutralized by adding 5.00 g of cation exchange resin and stirring for further 20 min, followed by filtration at 70°C . The volatile matters in the filtrate were removed by stripping for 2 h at 60°C under a pressure of 5 mmHg. A light yellow liquid product (APGE) was obtained in 95% yield.

Polyhydromethyl siloxane (PHMS) were prepared with D_4 , poly(methylhydrosiloxane) (Mw 3792) and hexamethyldisiloxane (MM) catalyzed by sulfuric acid. The method has already been reported in literature [18,19]. Thus, PHMS with 2, 4, 5, 6 and 8 Si—H bonds according to feed composition were obtained in 90% yield (Table 1).

Synthesis of polyglycerol-modified polysiloxane (APGE-PHMS)

Polyglycerol-modified polysiloxane (APGE-PHMS) were synthesized by the hydrosilylation reaction from APGE and PHMS with different Si—H groups. Five sets of APGE-PHMS systems were synthesized and the number of APGE contents was expected to be 2, 4, 5, 6 and 8 respectively. For example, APGE(5)-PHMS was synthesized as follow. In a 250 mL three-necked round bottom flask, 26.2 g (0.08 mol) APGE together with 14.9 g (0.08 mol, referring to the amount of Si—H-groups) PHMS ($m=5$, $n=5$) were dissolved in isopropanol. The mixture was heated to reflux under nitrogen atmosphere. The reaction was catalyzed by chloroplatinic acid. After 6 h, IR spectra showed complete disappearance of the Si—H bond. After completion of the reaction, the product was stripped at 60°C under a pressure of 5 mmHg to remove the volatile matters. A light yellow liquid product (APGE-PHMS) was obtained in 90% yield.

Characterization of structures

FT-IR spectra were measured using a Bruker V70 Fourier transform spectrometer (Germany) with a KBr plate. ^1H NMR and ^{29}Si NMR spectra were conducted with Bruker-400 MHz spectroscopy (Germany) at room temperature.

Measurement of solubility

Solubility was measured by dissolving APGE-PHMS directly in different solvents of various polarities at a concentration of 100 mg/mL at room temperature. There is no recognized standard to judge the polarity of solvent. We usually determine the polarity of the solvent according to the solvent dielectric constant. Thus, we choose seven solvents (isooctane, ether, methylene chloride, isopropanol, acetonitrile, dimethylsulfoxide, water) covering dielectric constant from 2 to 80 to carry out the experiment.

Measurement of equilibrium surface tension

The equilibrium surface tension of APGE-PHMS solutions was measured using a Krüss K12 Processor Tensiometer (Germany) and determined by the Wilhelmy plate method. The APGE-PHMS solutions were prepared by direct dissolution of APGE-PHMS in double distilled water. The length and thickness of the platinum plate were 19.9 mm and 0.2 mm, respectively. The dipping distance was 2 mm. The surface tension of the double distilled water was confirmed as being in the range of 72.0 ± 0.3 mN/m at $25.0 \pm 0.1^\circ\text{C}$, prior to measurements. The surface tension of each concentration was measured three times with an average deviation less than 0.2 mN/m at intervals of 90 s after stirring.

Measurement of dynamic surface tension

The dynamic surface tension was measured by a Krüss BP100 bubble-pressure Tensiometer (Germany). The solutions were also prepared by dissolving APGE-PHMS directly in double distilled water. This measurement was conducted with effective surface ages ranging from 10 to 200,000 ms.

Measurement of aggregation behavior

The aggregation behavior of APGE-PHMS solutions was monitored by dynamic light scattering (DLS) with a Zeta Plus Particle Size Analyzer (Brookhaven, USA) and the scattering angle was set at 90° . All of the solutions were filtered with a $0.45 \mu\text{m}$ (mixed cellulose acetate) membrane filter.

The structures of APGE-PHMS aggregates in solutions were also observed with a JEM-1011 (JEOL Co., Japan) transmission electron microscopy (TEM) by negative staining. A droplet of the surfactant solution was added onto a carbon-coated grid and allowed to equilibrate for 2 min. The removal of excess liquid was performed by blotting carefully with a filter paper. When the grid was partially dried, a drop of staining solution (2% phosphotungstic acid) was

Table 1
Composition of PHMS and their molecular weights.

Sample number	Feed composition		Expected Mn (g/mol)	Composition (^{29}Si NMR)		Mn based on ^{29}Si NMR spectra (g/mol)
	m	n		m	n	
1	8	2	874	8.38	1.49	872
2	6	4	846	5.76	3.15	777
3	5	5	832	4.82	4.10	765
4	4	6	818	4.24	6.25	851
5	2	8	790	1.70	7.83	758

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