



Effect of siloxane backbone length on butynediol-ethoxylate based polysiloxanes



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ABSTRACT

A series of butynediol-ethoxylate based polysiloxanes (PSi-EOs) with same composition but different lengths of siloxane backbone were designed and synthesized via hydrosilylation reaction. Their physicochemical properties and application performances have been discussed. With the increase of the length of siloxane backbone, the critical aggregation concentration (CAC) decreases and the surface tension at CAC (γ_{CAC}) increases, but the dynamic adsorption at the air/water interface has no significant change. Above the CAC, all of these three surfactants can self-assemble into spherical aggregates of 100 to 500 nm in aqueous solution. Moreover, the contact angle measurement on Paraffin film demonstrates that shorter siloxane backbone length of PSi-EO leads to lower contact angle and shows better spreading and wetting abilities. Using the foaming power test, PSi-EO with a longer siloxane backbone exhibits lower foaming and more effective anti-foaming properties in water.

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1. Introduction

Polysiloxane surfactants and acetylenic diol surfactants are classic nonionic surfactants that show quite predominant properties [1–4]. First, polysiloxane surfactants provide greater surface activity than acetylenic diol surfactants due to the distinctive flexibility of siloxane backbone [5,6]. Second, acetylenic diol surfactants show stronger hydrophilicity than polysiloxane surfactants because of the existence of ethylene oxide groups and two adjacent hydroxyl groups [7]. Third, classic acetylenic diol surfactants possess a carbon–carbon triple bond that can be directly attached to the siloxane backbone via hydrosilylation reaction [8]. The properties of these two types of surfactants are advantageous, which leads to a wide variety of potential applications in industry. In light of their different properties, the chemical combination of both polysiloxane and acetylenic diol in one molecule may be very interesting. However, acetylenic diol based polysiloxane surfactants have been reported surprisingly rarely [9–11].

In recent years, polysiloxane grafted with a polyether group has been greatly developed [12,13]. Such surfactants show excellent surface activity, outstanding spreading behavior and other remarkable properties, which is mainly attributed to the nature of siloxane backbone, such as extraordinary flexibility, high hydrophobicity, low cohesive energy, and low glass transition temperature [14]. In other words, the physicochemical properties of polysiloxane surfactants are significantly

affected by their siloxane backbone. Chung and Lim [15] synthesized twelve kinds of polydimethylsiloxane grafted with polyethyleneoxide, in which the surface properties were found to be sensitive to the size of hydrophobe (siloxane backbone). Zhang et al. [16] highlighted how the surfactant structure heavily influenced foam air flow by investigating the siloxane-polyether graft block copolymer series. It was observed that air flow of the foam increased as the siloxane backbone length decreased. Zhang et al. [17] discussed the role of siloxane surfactants by varying siloxane backbone length and polyether percentage in flexible polyurethane foam, which showed that surfactants with longer siloxane backbone provided higher film elasticity and better foam cell stability.

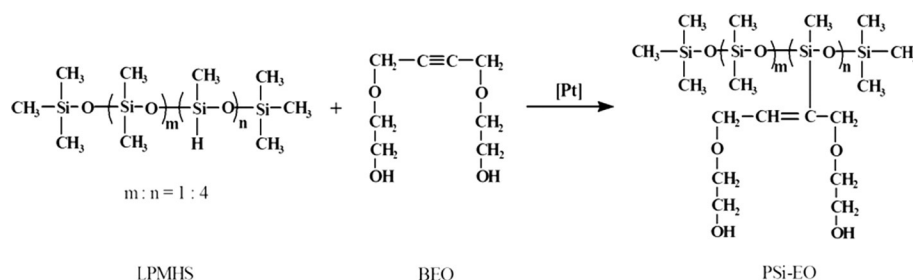
In this work, three butynediol-ethoxylate based polysiloxanes (PSi-EOs) with different siloxane backbone lengths were synthesized and characterized. The synthetic route is described in Scheme 1. The effect of siloxane backbone length of PSi-EO on their physicochemical properties and application performances was revealed by surface tension, transmission electron microscopy (TEM), contact angle, and foaming power measurements.

2. Materials and methods

2.1. Materials

Polymethylhydrosiloxane, octamethylcyclotetrasiloxane, hexamethyldisiloxane, 1,4-bis(2-hydroxyethoxy)-2-butyne (BEO) and hydrogen hexachloroplatinate (IV) hydrate (CPA) were obtained from Aladdin Reagent Co. (Shanghai, PR China). Isopropanol was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, PR China).

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Scheme 1. Synthetic route of butynediol-ethoxylate based polysiloxanes (PSi-EO).

All chemicals were used without further purification. Water used in all experiments was deionized water (18.2 MΩ).

2.2. Characterization

FT-IR spectra were obtained using a Bruker V70 spectrometer. ^1H and ^{29}Si NMR spectra were recorded on a Varian INOVA-400 Hz spectrometer using CDCl_3 as solvent and without the internal standard.

2.3. Synthesis

Low-hydrogen containing silicone oils (LPMHS) were synthesized using the method described previously [15,18]. The preparation of Speier's catalyst has been reported in detail elsewhere [19].

PSi-EOs were synthesized by hydrosilylation reaction of BEO and LPMHS in the presence of Speier's catalyst. In a 250 mL four-necked flask, BEO (50.0 g, 0.29 mol), LPMHS (25.0 g, 0.29 mol of Si-H groups), Speier's catalyst (2.0 mL) and isopropanol (50.0 mL) were added under a nitrogen atmosphere. The reaction mixture was continuously stirred at 120 °C for 4 h. After removal of isopropanol, a yellow transparent liquid was obtained (yield 95.0%).

FT-IR (KBr, cm^{-1}): 3391 (OH), 2962–2874 (CH), 1625 (CC), 1256 (Si-C), 1090 (Si-O-Si), 1060 (C-O-C).

^1H NMR (CDCl_3 , ppm): 6.2 (CEC-H), 4.2 (CC- CH_2), 4.1 (CH_2 -OH), 3.7 (CH_2 - CH_2 -OH), 3.5 (OH), 0.1–0.2 (Si- CH_3).

^{29}Si NMR (CDCl_3 , ppm): 9.8 (Si-(CH_3) $_3$), -18.6 (Si-(CH_3) $_2$), -34.9 (Si- CH_3).

2.4. Measurements

Equilibrium surface tension measurements were carried out on a Krüss K12 tensiometer (Krüss Company, Germany) using the Wilhelmy plate technique. Before the measurements, each PSi-EO/water system was equilibrated for 4 h. In general, the surface tension (γ) versus the logarithm of the solution concentration (C) profile was obtained at 25 ± 0.1 °C.

Measurements of dynamic surface tension were performed with a Krüss BP100 bubble-pressure tensiometer (Krüss Company, Germany) at 25 ± 0.1 °C. The effective surface ages were ranging from 10 to 100,000 ms.

Table 1

Composition, length of siloxane backbone, percentage of BEO branches and molecular weight of PSi-EO based on ^{29}Si NMR spectra.

Sample	Composition m/n	Length of siloxane backbone m + n	Percentage of BEO branches n/m + n	M_n (g/mol)
P5-20	5.8/20.4	26.2	0.78	5290.8
P8-32	8.2/29.6	37.8	0.78	7695.2
P10-40	9.9/36.7	46.6	0.79	9482.4

To investigate the micro-morphology of PSi-EO aggregates in aqueous solution, transmission electron microscopy (TEM) was performed with a JEM-1011 transmission electron microscope (JEOL Company, Japan). The working voltage was 100 kV. All sample solutions were deposited on a carbon-coated copper grid and negatively stained with 2 wt.% phosphotungstic acid. The samples were examined at 25 ± 0.1 °C.

The spreading and wetting abilities of PSi-EO solution over Paraffin film were studied by sessile drop method using a DSA 25 drop shape analyzer (Krüss Company, Germany) at 25 ± 0.1 °C. Paraffin film as hydrophobic substrate shows a contact angle for water: 106 ± 0.2 °.

The foaming power of PSi-EO solution (0.1 wt.%) was determined by Ross-Miles pour method at 40 ± 0.2 °C. The height of foam initially produced and the time of foam completely destroyed were measured.

3. Results and discussions

3.1. Synthesis of PSi-EO

The butynediol-ethoxylate based polysiloxanes (PSi-EOs) were successfully synthesized by hydrosilylation of LPMHS with BEO (Scheme 1). Their chemical structures were confirmed by FT-IR, ^1H NMR and ^{29}Si NMR. The disappearance of Si-H peak (2150 cm^{-1} in FT-IR spectra and 4.7 ppm in ^1H NMR) and appearance of CC peak (6.2 ppm in ^1H NMR) indicate the completion of hydrosilylation reaction. According to previous reports [15,18], the composition of PSi-EO can be exactly calculated by ^{29}Si NMR. Using the integral area values of trimethylsilyloxy, dimethylsilyloxy and methylhydrosilyloxy units, the values of m, n and molecular weight of PSi-EO are obtained (Table 1).

For PSi-EO, the ratio of m/n is 1/4, percentage of BEO branches is kept constant and length of siloxane backbone increases. As is shown in Table 1, the composition and molecular weight of PSi-EO are slightly different from the targeted values. And for larger molecules, a bigger difference is observed, which is considered due to the loss of raw material

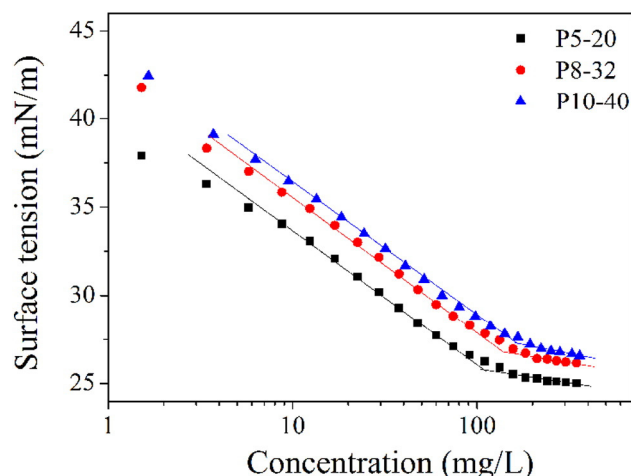


Fig. 1. Surface tensions as a function of $\log C$ for PSi-EO at 25 °C.

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