

# Synthesis and Properties of 4-( $\omega$ -Methoxyoligodimethylsiloxanyl)butyl Maleate: A New Surfmer

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**ABSTRACT:** Anionic reactive maleate with hydrophobic oligosiloxane chain was synthesized to use as a stabilizer in the batch and seeded emulsion polymerization of traditional monomers (acrylates, methacrylates, styrene, etc.). Polymerizable surfactant is obtained in a three-step synthesis, starting from the anionic polymerization of cyclic siloxanes, followed by the silylation of methanol with the obtained cyclic oligomer, and finishing with the acylation of the linear oligomer by maleic anhydride. The improved technique of the synthesis of 4-chlorobutoxydimethylchlorosilane, one of the initial substances for obtaining siloxane monomer, was elab-

orated. The anionic polymerization of octamethylcyclotetrasiloxane using cyclic alkoxy silane was carried out to form siloxane cyclic oligomer for the first time. The chemical structure of the monomer synthesized was confirmed by IR spectroscopy and functional analysis. Critical micelle concentration of the obtained surfactant was measured. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 310–313, 2004

**Key words:** anionic polymerization; macromonomers; ring-opening polymerization; silicones; surfactants

## INTRODUCTION

The use of surface active monomers (surfmers) in the processes of emulsion or dispersion polymerization permits us to obtain polymer colloidal systems in which the surfactants are permanently anchored onto the latex particle surfaces.<sup>1,2</sup> These systems should be stable over wide pH and temperature ranges as well as with regard to electrolytes. Polymer films with improved physicochemical and exploitational properties are formed on the basis of these latices. A surfmer molecule consists of hydrophilic and oleophilic parts as a conventional surfactant, and of a polymerizable group, as a rule, a carbon–carbon double bond. The hydrophilic groups may be both ionic (anionic or cationic) and nonionic (e.g., an oxyethylene chain of an appropriate chain length). Hydrocarbon chains (alkyl chains, alkyl phenol chains) or polypropylene oxide and polybutylene oxide chains are used as hydrophobic molecule parts. Siloxanes are known to possess strong hydrophobic properties and organic silicon surfactants are known to be very effective stabilizers of suspension polymerization.<sup>3</sup> Nevertheless, there is no information about the synthesis and the use of surface active monomers that contain siloxane fragments as a hydrophobic molecule part. On the other hand, maleic surfmers are known to have an addi-

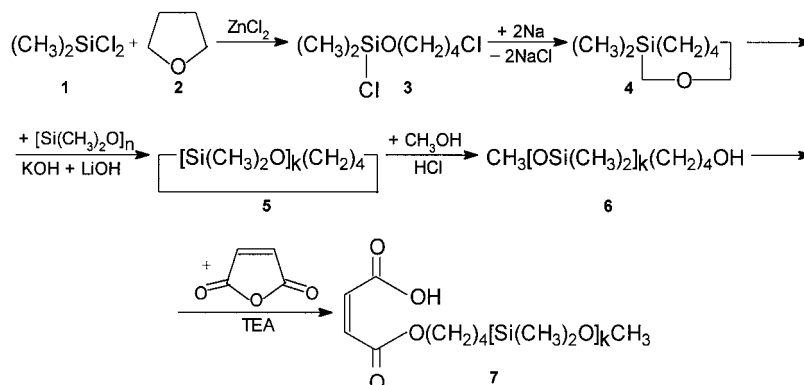
tional advantage over other surface active monomers. They do not undergo homopolymerization<sup>4</sup> and this means that the surfmers do not produce water-soluble polymers (polysoaps) in the aqueous phase.<sup>5</sup> However, they copolymerize with other monomers. Maleic surfmer is covalently anchored onto the surface of the polymer particles during the emulsion or dispersion polymerization process and therefore practically it is not incorporated into the polymer phase.

This work is devoted to the synthesis and the surface active characterization of maleic high-molecular-weight monomer (macromonomer) containing oligosiloxane substituent. This kind of anionic polymerizable surfactants seems to be promising for use in adhesives, coatings etc.

## RESULTS AND DISCUSSION

4-Chlorobutoxydimethylchlorosilane (**3**) was used as one of the initial substances to obtain organic silicon monomers. The methods of obtaining it are described in the literature. According to the first method the main product (**3**) is obtained by the interaction of dichlorodimethylsilane (**1**) with tetrahydrofuran (**2**) without a catalyst in an autoclave at 200°C.<sup>6</sup> According to the other method,<sup>7</sup> 4-chlorobutoxydimethylchlorosilane (**3**) was obtained (65% yield) by heating dichlorodimethylsilane (**1**) and tetrahydrofuran (**2**) with zinc chloride (molar ratio 2 : 1 : 0.018, respectively). The deficiencies of these methods are hard reaction conditions in the first case and the necessity of

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using a twofold excess of dichlorodimethylsilane (1) in the second one. We have elaborated the method of synthesis that allows the formation of 4-chlorobutoxydimethylchlorosilane (3) under mild conditions with higher yield. Dichlorodimethylsilane (1) and tetrahydrofuran (2) were boiled with zinc chloride (molar ratio 1 : 1 :  $7.58 \times 10^{-4}$ , respectively) under reflux for 20 h and the reaction mixture was distilled in vacuum. Purposefully 4-chlorobutoxydimethylchlorosilane (3) was obtained (71% yield). Its structure was confirmed by the elemental analysis data and the physicochemical constants conformed to literature data.<sup>7,8</sup>

2,2-Dimethyl-1-oxa-2-silacyclohexane (4) was obtained by heating the substance (3) with metallic sodium.<sup>8</sup> Acyclic alkoxy silanes are known to be used in the anionic polymerization of dimethylcyclotetrasiloxanes;<sup>9</sup> however, the information about the possibility of the use of the cyclic alkoxy silanes with the same purpose was not found. The anionic polymerization of octamethylcyclotetrasiloxane [ $\text{Si}(\text{CH}_3)_2\text{O}$ ]<sub>n</sub>,  $n = 4$  by 2,2-dimethyl-1-oxa-2-silacyclohexane (4) (a cyclic alkoxy silane) was carried out to produce a cyclic siloxane oligomer (5) where  $k \approx 9$ . The process was performed in the presence of a catalytic amount of the powdered alkalis (KOH or LiOH) at 120°C; molar ratio of 2,2-dimethyl-1-oxa-2-silacyclohexane : octamethylcyclotetrasiloxane was 2 : 1. The course of the reaction was controlled by the change of the molecular weight of the reaction mixture. The polymerization process was finished when the molecular weight reached 700–750 g/mol. The temperature was increased to 150°C if the molecular weight increased slowly. The linear oligomer (6) 4-( $\omega$ -methoxyoligodimethylsiloxanyl)-1-butanol was synthesized by the interaction of the cyclic oligosiloxane (5) with methanol. The siloxane macromonomer (7) 4-( $\omega$ -methoxyoligodimethylsiloxanyl)butyl maleate was obtained by the acylation of the oligomer (6) by maleic anhydride.

The structure of the macromonomer (7) was confirmed by IR spectroscopy and functional analyses data. The infrared spectrum of the surfmer (7) is presented in Figure 1.

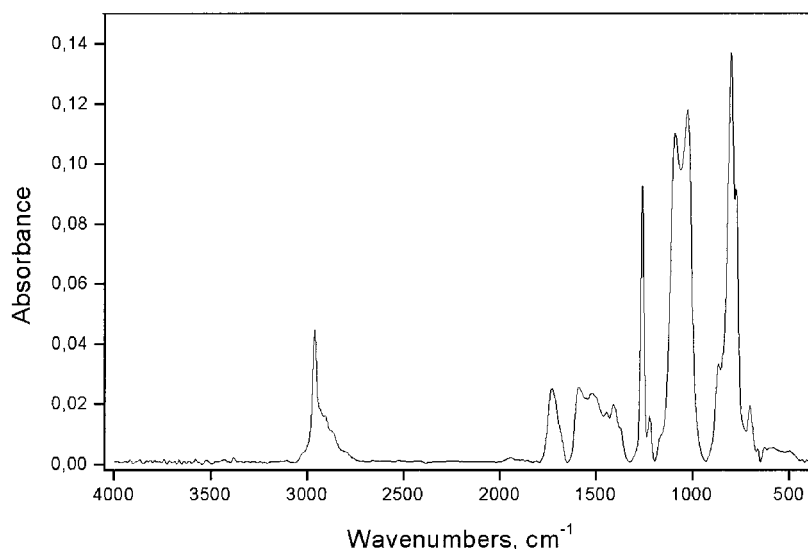
Present in the IR spectrum are a very intensive duplet of absorption bands at 1,025 and 1,090  $\text{cm}^{-1}$  attributable to the valency oscillation of the Si–O bond; as well as very intensive absorption bands at 1,260 and 800  $\text{cm}^{-1}$  due to the deformation oscillations of the methyl substituents of  $\text{Si}(\text{CH}_3)_2$ ; and an absorption band of medium intensity at 1,590  $\text{cm}^{-1}$  resulting from valency oscillations of the C=C bond conjugated with C=O. The broad absorption near 703  $\text{cm}^{-1}$  suggests a  $-(\text{CH}_2)_n-$  group in which  $n > 3$  and corresponds to the pendulum oscillations of  $\text{CH}_2$ . Carbonyl groups are displayed as a broken intensive absorption band at 1,700, 1,720, and 1,740  $\text{cm}^{-1}$ ; the C–O bond of the ester group corresponds to duplet of absorption bands at 1,150 and 1,220  $\text{cm}^{-1}$ ; while the O–H carboxyl group corresponds to wide absorption band in the range 2,750–3,100  $\text{cm}^{-1}$ .

The isotherm of the surface tension of potassium salt of the macromonomer (7) measured at 20°C is presented in Figure 2. The surface tension was determined with a du Noüy ring tensiometer. The critical micelle concentration (cmc) was found ( $2.21 \times 10^{-3}$  % w/w) and the surface tension at the cmc was determined ( $\sigma_{\text{cmc}} = 40.0$  mN/m). Potassium salt of the investigated macromonomer is obviously a surface active substance, since the surface tension of water decreases when the surfactant is added.

The surface tension decreases almost linearly with increasing surfmer concentration and becomes constant above a certain concentration, which evidently corresponds to the cmc.

## EXPERIMENTAL

Dichlorodimethylsilane and tetrahydrofuran from Aldrich were distilled under atmospheric pressure just before use. Methanol from Aldrich was dried by boiling with magnesium chips under reflux for 2–3 h and distilled. Butanone from Aldrich was dried over  $\text{CaCl}_2$  and distilled. Maleic anhydride from Aldrich was purified by vacuum distillation and kept under argon. All the other materials from Aldrich—zinc chloride,



**Figure 1** The infrared spectrum of 4-( $\omega$ -methoxyoligodimethylsiloxanyl)butyl maleate.

acetic acid, hydrochloric acid, and sodium—or from Merck—triethylamine, potassium hydroxide, and lithium hydroxide—were used as supplied commercially.

#### 4-Chlorobutoxydimethylchlorosilane (3)

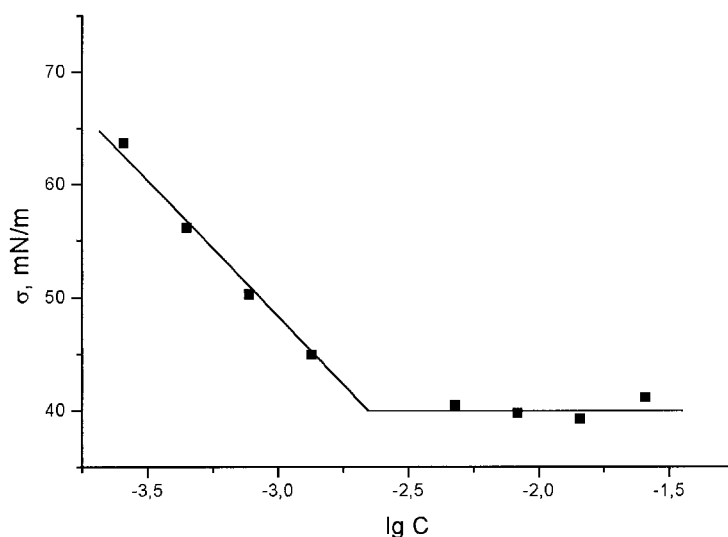
The mixture of dichlorodimethylsilane (1) (62.5 g, 0.484 mol), tetrahydrofuran (2) (34.9 g, 0.484 mol), and  $\text{ZnCl}_2$  (0.05 g,  $3.67 \times 10^{-4}$  mol) was boiled under reflux for 20 h. Distillation gave 69.2 g (71% yield) of 4-chlorobutoxydimethylchlorosilane, bp 88–91°C/10 mm Hg (refer. 64°C/4.2 mm Hg),<sup>8</sup>  $n_D^{20}$  1.4354 (refer. 1.4365).<sup>7</sup> Found, %: C 35.95; H 7.65; Cl 34.70;  $\text{Cl}_{\text{act}}$  17.94; Si 13.13. Calculated, %: C 35.82; H 7.01; Cl 35.24;  $\text{Cl}_{\text{act}}$  17.62; Si 13.96.

2,2-Dimethyl-1-oxa-2-silacyclohexane (4) was synthesized by heating 4-chlorobutoxydimethylchlorosilane (3) with metallic sodium according to the technique described elsewhere.<sup>8</sup>

Octamethylcyclotetrasiloxane was synthesized by the hydrolysis of dichlorodimethylsilane (1) by the described method.<sup>10</sup>

#### Cyclic siloxane oligomer (5)

The mixture of octamethylcyclotetrasiloxane (18.2 g, 0.061 mol), 2,2-dimethyl-1-oxa-2-silacyclohexane (4) (4.0 g, 0.031 mol) and powdered LiOH (0.05 g,  $2.1 \times 10^{-3}$  mol) was stirred and boiled under reflux with a calcium chloride tube for 30 h. Powdered LiOH



**Figure 2** Plot of surface tension  $\sigma$  versus siloxane macromonomer concentration in water.

(0.055 g,  $2.3 \times 10^{-3}$  mol) was added and the reaction mixture was heated to 120–150°C and stirred for about 36 h until the molecular weight reached 700–750 g/mol (cryoscopically in benzene). The reaction mixture was cooled to room temperature. Glacial acetic acid (0.27 g,  $4.5 \times 10^{-3}$  mol) was added to neutralize LiOH over a 1-h period to a rapidly stirred reaction mixture. Lithium acetate formed was filtered. To remove water evolved during neutralization and the initial nonreacted substances, the reaction product was heated to 150°C under reduced pressure (10 mm Hg). The molecular weight of the synthesized oligomer was 749 g/mol (cryoscopically in benzene).

#### 4-( $\omega$ -Methoxyoligodimethylsiloxanyl)-1-butanol (6)

Concentrated hydrochloric acid (0.020 mL) was added to the rapidly stirred heterogeneous mixture of cyclic oligomer (5) (18.8 g, 0.026 mol) and methanol (2.5 g, 0.078 mol). Besides the reaction mixture became homogeneous and its viscosity decreased sharply. After standing 36 h, triethylamine (0.024 g,  $2.4 \times 10^{-4}$  mol) was added to neutralize HCl. Excess methanol was removed under reduced pressure (10 mm Hg) and the residue was kept for 2 h at 0.1 mm Hg. Triethylammonium hydrochloride precipitate was filtered. The experimentally found hydroxyl value was 42.6 mg KOH/g.

#### 4-( $\omega$ -Methoxyoligodimethylsiloxanyl)butyl maleate (7)

The solution of 4-( $\omega$ -methoxyoligodimethylsiloxanyl)-1-butanol (6) (18.7 g), maleic anhydride (1.4 g, 0.014 mol), and triethylamine (3.6 mg,  $3.6 \times 10^{-4}$  mol) in butanone (22 mL) was boiled under reflux for 14 h. The solvent was removed under reduced pressure (10 mm Hg) and the residue was kept for 2 h under pressure at 0.1 mm Hg. The experimentally found acid number was 43.8 mg KOH/g; molecular weight of siloxane macromonomer (7) was determined cryoscopically in benzene as 1,281 g/mol.

#### Methods of analysis

Hydroxyl value of 4-( $\omega$ -methoxyoligodimethylsiloxanyl)-1-butanol (6) was determined by the method of acetylation by acetic anhydride in pyridine catalyzed by perchloric acid.<sup>11</sup>

The acid number of the macromonomer (7) was determined by the titration with 0.1N KOH solution in the presence of phenolphthalein.

IR spectra were carried out in  $\text{CHCl}_3$  solution with a RS 1000 FT-IR spectrometer (UNICAM Analytische System GmbH).

A weighed portion of the macromonomer (7) was dissolved in water containing an equimolar amount of KOH to measure the surface tension.

The molecular weight of the synthesized substances was determined by means of cryoscopic analysis,<sup>12</sup> based upon the lowering (depression) of the freezing point of a pure substance (the solvent) by the addition of the studied compound (the solute) to that substance. So, freezing points of both pure benzene and benzene solution of the studied compound were determined with a precision of 0.003°C. The solute concentrations were 0.25–1.3% w/w. The equation<sup>13</sup> was used to calculate approximate molecular weights from freezing point depression data.

#### CONCLUSION

The anionic polymerization of octamethylcyclotetrasiloxane using 2,2-dimethyl-1-oxa-2-silacyclohexane followed by the interaction of the obtained cyclic oligomer with methanol and subsequent acylation of the obtained linear oligomer containing hydroxy group by maleic anhydride is a preparative method for new surface active monomer synthesis. The method of the 4-chlorobutoxydimethylchlorosilane synthesis was improved. The anionic polymerization of octamethylcyclotetrasiloxane by a cyclic alkoxysilane was carried out for the first time.

The obtained surfmer is characterized by IR spectroscopy, functional analysis, and cmc. The cmc value is very small ( $2.21 \times 10^{-3}$  % w/w) because of the long hydrophobic siloxane chain.

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