Research Article

Synthesis of Polymeric Surfactant with Polymethylsilicone Backbone which is Grafted with a Sugar

Şeker Kısımları ile Graftlanmış olan Polimetilsiloksan Bazlı Polimerik Yüzey Aktif Madde Sentezi

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Abstract

The enofuranose derivative (1) that was thought to be suitable for reaction with polymethylhydrogensiloxane was synthesized by hydrosilylation reaction in the presence of a platinum catalyst. Allyl group was introduced to the protected sugar derivative, which were further used for bonding these molecule to silicone oligomer through double bond addition. The polymeric surfactant (2) has been prepared using a polymethylsilicon backbone grafted with a glucose moiety. The synthesized compounds **1** and **2** were characterized by nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR).

Keywords: Surfactants, Biosurfactants, Polymethylsilicon, Sugar based surface active agents

Öz

İlk olarak, platin katalizörü varlığında hidrosililasyon reaksiyonuna girebilen enofuranoz türevi (1) hazırlandı. Sentezlenen enofuranoz türevinin allil grubunun çifte bağından silikon oligomerine bağlanması gerçekleştirildi. Polimerik yüzey aktif madde (2) şeker kısımları ile graftlanmış olan bir polimetilsilikon bazlı malzeme kullanılarak hazırlandı. Sentezlenen **1** ve **2** nolu bileşiklerin yapıları, Nükleer Manyetik Rezonans (NMR) ve FITR spektroskopisi ile aydınlatıldı.

Anahtar Kelimeler: Yüzey Aktif Madde, Biyolojik Yüzey Aktif Maddeler, Polimetilsiloksan, Şeker Bazlı Yüzey Aktif Maddeler

1. Introduction

Surfactans have very important roles in our everday life. They have many applications in almost every chemical industry, such as detergents, paints, dyestuffs, paper coating, inks, plastics and fibers, personal care, cosmetics, agrochemicals, pharmaceuticals and food processing. etc. In addition, they play a vital role in the oil industry, e.g. in enhanced and tertiary oil recovery, oil slick dispersion for environmental protection. It is important to choose the right molecule for a specific application, so it is essential to understand the basic phenomena involved in any application (Tadros et al. 2005).

Basically, the classification of surfactants based on the nature of the hydrophilic group is commonly used. According to, this classification, a surfactant can be either ionic, non ionic and special (Os Van et al. 1993). The special surfactans are quite different from the conventional ones, because they have certain unquie properties such as lower surface tension, distinctive oil and water solubility and high wetting caharacteristics, etc. They were classified mainly three groups are fluorocarbon, silicone and polymeric surfactants.

Silicone surfactants, sometimes refferred to as organosilicones, are those with a poly(dimethyl siloxane) backbone. They are prepared by incorporation of a water soluble or hydrophilic group into a siloxane structures. An example of the organosilicone is polyoxyethylene polymethyl siloxane (Figure 1). The mechanism by which these molecules lower the surface tension of water to low values is far from well understood. The surfactants are widely applied are spreading agents on many hydrophobic surface (Hill 1999). The new types of amphiphilic polysiloxane diblock copolymers containing a pure polysiloxane backbone were prepared by the functionalization of poly(dimethylsiloxane)-*block*-poly-(methylvinylsiloxane) copolymers (Bauer et al. 2000). And also, new, but straightforward method for the modification of the vinyl-functional block via hydrosilylation with different Si-H-containing molecules had been applied, leading

to a variety of "all silicone" block copolymers (Boehm et al. 2012).

Lin and Chen designed some cleavable modified silicone surfactants. A series of cleavable water-soluble silicone surfactants were prepared by the reaction of a hydroxyl-terminated polyester and an organopolysiloxane. The cleavable surfactants can decompose into water insoluble moiety of a silanol and to a water soluble product under acidic conditions, whereas these compounds are stable under neutral or alkaline conditions. The cleavable surfactants may degrade into non-surface active species or into new surface-active compounds with different properties by chemical means (Lin et al. 2006).

Polymeric surfactants have recently been interested area due to wide range of applications and unique properties for dispersions, suspensions and emulsions. Silicone surfactants may also be considered as polymeric. However, the recent development of special polymeric surfactants of graft type is also known as comb-like polymers. These have enabled one to obtain specific applications in dispersions (Raffa et al. 2015, Liu et al. 2001)

Nonionic, anionic and amphoteric Sucrose-based surfactants have been synthesized by both chemical and enzymatic paths with special focus on methods for the regioselective synthesis of carbohydrate based surfactants (Andersson et al. 2006, Bazitoet al. 2001). These are compatible with skin. They elicit little or no irritation, suggesting applications in cosmetics including skin preparations, eyelash products, cosmetic oil gels and deodorant formulations. They have also been used as plasticizers and as antistatic agents in plastics (Polat et al. 2001).

The number of studies on the carbohydrate-modified siloxanes increase day by day. The idea is to combine the extraordinary surface activity and wetting properties of siloxanes with the biodegradability of carbohydrates. Some years ago, alkyl polyglycosides were firstly synthesized and now they are common surfactants for different applications. Binding of siloxanes and carbohydrates can be achieved by means of glycosyl bonds (Si-C) with or without a spacer. The patent published by Wacker Chemie GmbH describes the hydrosilylation with 1-allyl glycildly eter-6-maleate-D-glucose and 2-hydrogen-tri(methylsiloxane) which gives a white solide with a good solubility in water (Figure 2) (Sejpka et al. 1994).

Some carbohydrate derivatives were prepared for usage as hyrophilic head groups for some surface-active agents

(Reinsborough et al. 2004, Retailleau et al. 1998, Abert et al. 2002, Han et al. 2012). Nowadays, carbohydrate-modified polysiloxane bola surfactants of different molecular weight were synthesized by two-step reactions (Zeng et al. 2015). Hydrophilic sugar moieties can provide solubility or dispersion in water, depending on the size and the nature of the sugar and non-sugar parts. Hydrophobic groups were
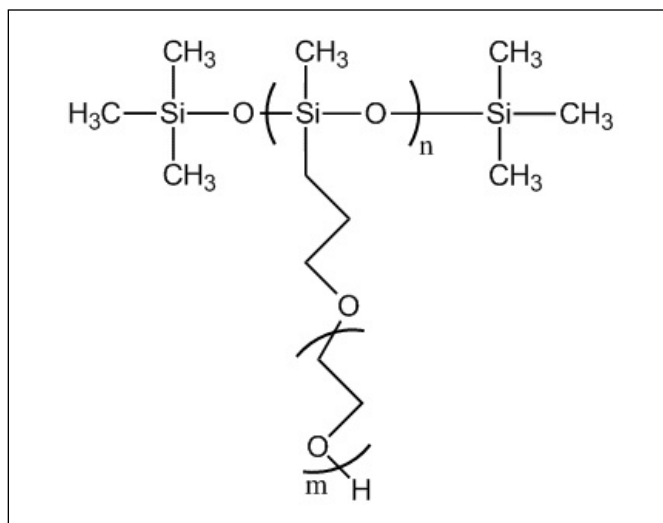

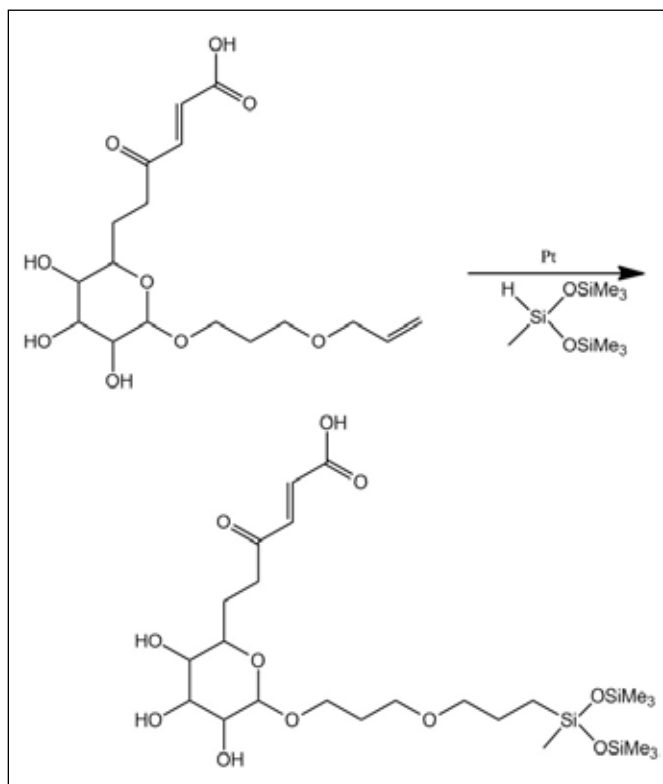**Figure 1.** Sturcture of a silicon surfactant.

Figure 2. An example carbohydrate-modified siloxane.

introduced by the reaction of free hydroxyl groups on the protected sugar, either by direct etherification with the use of allyl halides. Allyl groups were introduced to the protected sugar derivatives which were further used for bonding these molecules to some siloxane oligomers through double bond addition.

Carbohydrates are widely available and relatively cheap. In fact, surfactants produced from carbohydrates, referred to as carbohydrate surfactants, have been known to exist for a long time. They are renewable, biocompatible, biodegradable, nontoxic, and less irritating (Hill et al. 2009). It is therefore particularly advantageous to combine siloxane with carbohydrates to develop carbohydrate-modified siloxane surfactants. Such surfactants have been previously reported in the literature and successfully used to increase solubility for hydrophobic drugs, enhancing transdermal penetration of drugs, improving cosmetic formulation, and etc. For these advantages, we aimed to procedure a novel carbohydrate-modified siloxane surfactant. It is also a non-ionic and polymeric surfactant with a polymethylsilicone backbone which is grafted with a glucose moiety. For this purpose, enofuranose derivative of glucose (**1**) synthesized by a hydrosilylation reaction in the presence of a platinum catalyst.

2. Material and Methods

2.1. Materials

Solvents were dried with molecular sieves (4 °A) for at least 24 h prior to use when required. When dry conditions were required, the reactions were performed under Ar or N_2. All solvent removals were carried out under reduced pressure. TLC and column chromatography were performed on precoated aluminium plates (Merck 5554) and silica gel G-60 (Merck 7734), respectively. The spot of TLC were developed by spraying 5 % aqueous sulphuric acid and by heating the plates above 120 °C for about 3 minutes. All ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz (^{1}H) and at 100.57 MHz (^{13}C) with a Varian Mercury instrument. Chemical shifts are reported in ppm downfield from TMS as an internal standard; J values are given in Hz. IR spectra were recorded on a Perkin Elmer 100 FTIR spectrometer. Optical rotations were determined using a Rudolph Research Analytical Autopol I automatic polarimeter.

2.2. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2'-propene-1'-yl)-α-D-glucofuranose (1)

NaH (%60, 0.7g, 17.4 mmol) was suspended in dry THF

(5mL) under N_2 at 0°C. A solution of the 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (Diacetoneglucose) (3 g, 11.6 mmol) in THF (30 mL) was added dropwise using a dropping funnel and the mixture was stirred for 30 min at r.t. Allyl bromide (2.2 mL, 24 mmol) was added slowly at 0°C. Then, the mixture was heated under reflux for 6h. After the end of this period, saturated NH_4Cl was added very slowly at at 0°C and the solution was extracted with CH_2Cl_2 (3x50 mL), dried over anhdrous Na_2SO_4 and filtered. The filtrate was concentrated to give a yellow syrup. The crude syrupy product was purified by column chromatography to give the allyl derivative **1** of the corresponding sugar as a yellow syrupy (3.55g, yield 96%) (Figure 3.). $[\alpha]^{18}_D$= -30.2, (c 0.9, CH_2Cl_2); IR (cm^{-1}) υ^{film}_{max} 3080 (=C-H), 2983, 2945, 2873 (C-H), 1647 (C=C), 1076 (C=CH_2) (Shing, 2002).

2.3. Synthesis of Polymethylglucosiloxane (2)

To a stirred solution of PMHS (0.11 g, 0.0485 mmol) and 35 equlavents of compound **1** (0.47g, 1.56 mmol) in dry toluene (25 mL) was added H_2PtCl_6 (0.5 mL) as a solution in isopropylalcohol (0.2%) under N_2 at r.t (Lewis 1991, Lichtenhan 2005). The mixture was heated at 100 °C. The
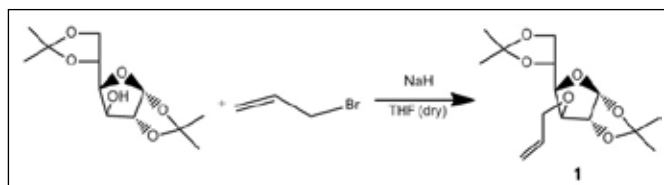

Figure 3. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2'-propene-1'-yl)-α-D-glucofuranose (**1**).
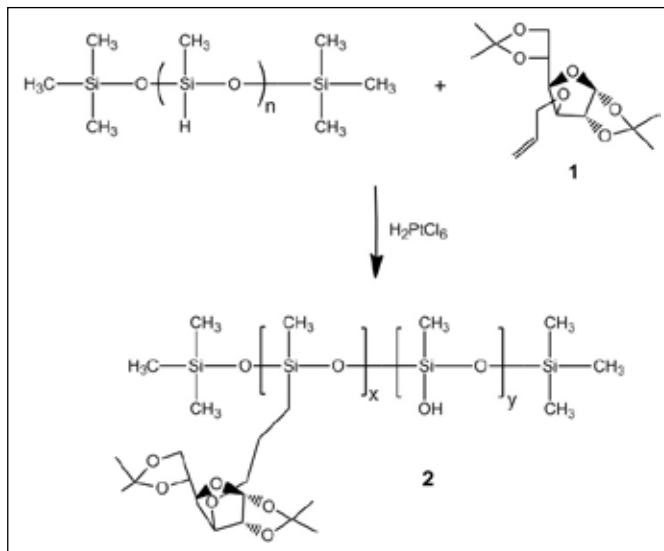

Figue 4. Synthesis of polymethylglucosiloxane (**2**).

viscosity increased during the reaction. After 24 h, NaOH solution was added to stop reaction. The solution was extracted with CH_2Cl_2 (3x50 mL), washed with water (2x50 mL), dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to give very viscous syrup (**2**) (Figure 4.). The IR spectrum indicated the disappearance of the Si-H bond absorbance at (2164 cm^{-1}) which is indicative of the reaction.

3. Results and Discussion

The aim of our study investigate the possibility of producing glucose based compounds which might have some surfactant properties. Glucose is one of the most abundant, sustainable natural compound and it can provide the hydrophilic "head" section to surfactants. These alkylglucosides are very important compounds because they can be produced economically and there is no need to protect the sugar molecule. It is no possible to make many derivatives of sugars without using the protecting groups. Thus, we decided to use a diacetone derivative (1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose) as starting glucose. Diacetone-D-glucose can be cheaply produced from glucose and acetone in the presence sulphuric acid as catalyst. Diacetone-D-glucose has only one free hydroxyl group therefore it is more convenient to use. This free hydroxyl group on C-3 of the glucose can be easily converted to the etheric group (Telli 2015). Therefore we decided to make some long chair ethers. We prepared allyl (**1**) ethers, using allyl bromide. The ^{1}H NMR spectral data of compound **1** is at Table 1.

In order to obtain surfactant properties, isopropylidene protecting groups must be removed since they make sugar

molecule hydrophobic also. Removal of isopropylidene groups is achieved by the hydrolysis in the presence of hydrofluoric acid. This acid completely removes the isopropylidene groups. Using less strong acids will remove the 5,6-isopropylidene rings completely.

Polymethylhydrogensiloxane is an oligomer that was obtained from Merck. The manufacturers claim that it has an average of 35 siloxane groups between two trimethylsilyl terminal groups. According to the manufacturers claim, the siloxane oligomer contains a total of 41 methyl groups and 35 Si-H protons. Thus it includes a total of 123 methyl protons and 35 Si-H protons. The ratio of these protons: 123/35 = 3.5. ^{1}H NMR spectrum of the siloxane oligomer indicates Si-Me group signals (singlets) at δ 0-0.2 (two small peaks for terminal methyl groups and a big one for the siloxane (-O-Si(CH$_3$)O-) methyl groups and also a Si-H singlet at δ 4.72. In the spectrum, the ratio of the integral curves (integration of the total Me groups signals / Si-H bond proton) is 12/3 = 4. This indicates that the oligomer containes less than 35, about 30 siloxane groups.

Reaction of oligomer with the compound **1** was carried out with a large excess of the compound **1** since we did not how many sugar groups would be bonded to oligomer. During the chromatographic purification, unreacted compound **1** eluted from the column first and the reaction product eluted rather late. Since the product has very complicated structure, its ^{1}H NMR spectra are also complicated. However, it is possible to obtain some important information related to the structure. Thus, ^{1}H NMR spectrum of the reaction product indicates the absence of the Si-H bond singlet. This is due to the hydrolysis of the remaining Si-H bonds at the

Table 1. ^{1}H NMR spectral data of the compound 1.

Positions of atoms	^{1}H NMR (δ)	H and J couplings (Hz)
H-1	5.87 d	1 H, $J_{1,2}$=3.6
H-2'	5.88 m	1 H
H-3'	5.29 m	1 H, $J_{2',3'}$(trans)=16.0
H-3'	5.18 m	1 H, $J_{2',3'}$(cis)=12.0
H-2	4.53 d	1 H
H-5	4.30 dt	1 H, $J_{1,2}$=3.6
H-4, H-6a, H-1'	4.20-4.05 m	4 H
H-6b	3.98 dd	1 H, $J_{5,6b}$=6.0
H-3	3.93 d	1 H, $J_{2,3}$=3.2
Me	1.48 s	3 H
Me	1.41 s	3 H
Me	1.34 s	3 H
Me	1.30 s	3 H

end of the reaction, with sodium hydroxide solution, which were converted to hydroxyl groups. Low field part of the spectrum (between δ 6.2 and 3.2) contains no Si-Me signals and H-2' methylene proton signals (C-CH$_2$-C group on the grafted side chain). The remaining low field signals are due to the sugar protons (except the isopropylidene methyls) and also Si-CH$_2$ (H-3') and 3-O-CH$_2$- (H-1') group on the sugar. H-1 and H-2 characteristic signals of the furanose ring are easily detectable at δ 5.86 and 4.53 (resolution is not good since the structure of polymeric. When we accept the integration of these protons as one proton each, we find a total of 11 protons. The grafted side chain (only one) indeed contains 11 protons, excluding the C-CH$_2$-C group on the grafted side chain which appear at the high field. It is important to mention that the spectrum contains only a trace of double bond signals of the compound **1**. These results are indicative that the sugar moity is actually bonded to the siloxane backbone. Now the question, of how many sugar groups were bonded to the parent siloxane oligomer, remains. We can roughly calculate the number of the grafted sugar groups from the ratio of the integration curves. The high field part of the spectrum contains more methyl groups and some methylene groups now, since isopropylidene methyl groups and C-CH$_2$-C group protons were also added to the total Si-Me protons. In the spectrum, the largest Si-Me signal is found at δ 0.09 this must be due to the (-O-Si(CH$_3$)O-) methyl protons. The high field shift is probably due to the sterical effects of the sugar side chains. If we accept that there are 30 (-O-Si(CH$_3$)O-) groups on the siloxane back-bone, this sumps up to 90 protons. Integral of these protons is 2,5 cm. Integral of the low field part of the spectrum is measured as 5,4 cm. If 2,5 cm is equal to 90 protons, 5,4 cm will be equal to 194 protons. If we divide this number with the number of the low field protons in one sugar unit we find the number of ~18. This calculation with an approximation indicates that very roughly about 17-18 sugar units are bound to he back-bone polymer. This means almost half of the siloxane groups were grafted.

In the FTIR spectrum of the 1,2:5,6-Di-O-isopropylidene-3-O-(2'-propene-1'-yl)-α-D-glucofuranose (**1**), the characteristic absorbtions for C=C (allyl) and COC (ether) groups were observed approximately 1647 and 1150 cm^{-1}, repectively. In the spectrum of (**1**) the hydroxyl (OH) peak at 3350 cm^{-1} was disappeared (Telli 2015). Besides, in the FTIR spectrum of the Polymethylglucosiloxane (**2**), the peaks at 1261, 838 cm^{-1} and at 1022, 1096 cm^{-1} were attributed to Si–C groups and Si–O–Si groups, respectively. It was also seen that allyl (C=C) peak at 1647 cm^{-1} was lost (Zeng et al. 2015).

4. Conclusions

The reaction between a non-ionic polymeric surfactant and a polymethylsilicon backbone which is grafted with a glucose moiety was performed. The polymeric surfactant (**2**) has been prepared using the enofuranose derivative (**1**). We have found out that these reactions could be monitored easily by observing the decrease of the characteristic sharp peak of the Si-H absorbtion at 2166 cm^{-1} on the FTIR spectra. Thus the formation of the compound **2** from the siloxane oligomer and the compound **1** was monitored by this method.

The new carbohydrate-modified siloxane derivate (polymeric surfactant) was synthesized. It is to combine the extraordinary surface activity and wetting properties of siloxanes with the biodegradability of carbohydrates. This advance can be expanded the application of siloxane surfactants into new fields.

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