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Silicon-Modified Carbohydrate Surfactants VI: Synthesis of Carbosilane, Silane, Polysilane and Non-permethylated Siloxane Derivatives; the Wetting Behaviour of Epoxy-modified Precursor Liquids on Non-polar Surfaces*

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The synthesis of carbohydrate surfactants bearing carbosilane, silane, polysilane and non-permethylated siloxane moieties is described. These surfactants consist of three structural elements: (1) a silicon-containing moiety, (2) a spacer and (3) a carbohydrate unit. Additionally two different types of mixed structures have been synthesized: (a) single-chained carbosilane–siloxane surfactants and (b) double-chained combinations of carbosilanes, silanes and siloxanes. The wetting behaviour of the key intermediates, the allyl glycidyl derivatives, has been investigated by static surface tension (γ_{lv}, σ) and wetting tension ($\gamma_{sv} - \gamma_{sl}$, α) measurements on a non-polar perfluorinated surface (FEP® plate). The contact angles obtained for these pure liquids are not a linear function of the surface tension but depend on the polarity of the substructures. © 1998 John Wiley & Sons, Ltd.

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1 INTRODUCTION

In preceding papers[1–6] we have described synthetic routes yielding defined carbohydrate-modified siloxane surfactants in a few regioselective steps with high yields. According to this concept, low-molecular-weight derivatives consist of four independent structural elements: (1) a siloxanyl moiety, (2) a spacer, (3) a carbohydrate unit and (4) a modifying element (Fig. 1).

Systematic derivatizations allowed an evaluation of the impact of all four structural elements on the equilibrium wetting properties (equilib-

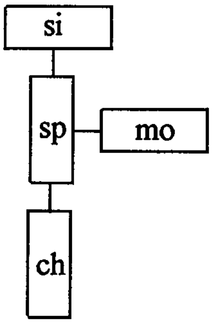

Figure 1 The structural elements of a carbohydrate-modified siloxane surfactant: si, siloxanyl moiety; sp, spacer; ch, carbohydrate unit; mo, modifying element.

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rium contact angle, surface tension and solid/liquid interfacial tension) of dilute aqueous surfactant solutions on low-energy, non-polar solid surfaces. It was found[7] that permethylated siloxanyl moieties possess a high capacity to level out the impacts of the other structural elements. Nevertheless, bulky carbohydrate units and certain methyl groups containing modifying elements can influence the wetting behaviour considerably. Due to the dominant role of the siloxanyl moiety, the wetting properties of surfactant solutions react sensitively to changes of the siloxane structure.

Therefore we started a systematic investigation[8] of the wetting properties of different silicon-containing liquid precursors (siloxanes, carbosilanes, silanes and polysilanes). As expected from the few data available in the literature, the backbone type, as well as the substituents at silicon,[9–12] influences the energy balance and the wetting process. We found that on a non-polar perfluorinated surface siloxanes form a higher contact angle than silanes or hydrocarbons of the same surface tension.

Surface-active carbosilanes, silanes and polysilanes have been described in only a few cases. The interest in carbosilanes[13, 14] stems from their superior hydrolytic stability. Aside from the well-known reactive trimethoxysilyl derivatives for surface protection applications,[15–18] certain trimethylsilyl-substituted surfactants[19, 20] have attracted attention because of their excellent spreading properties. In an attempt to prepare semiconducting thin films, polysilanes bearing hydrophilic side chains have frequently been used.[21–24] Surface-active polysilanes have also been claimed as defoamers in photographic layers.[25, 26] In a single paper,[27] surface tensions and spreading coefficients of oligo-oxyethylene-modified siloxane, carbosilane and polysilane derivatives (with a broad molecular weight distribution) have been compared.

It is the purpose of this paper to describe the synthesis of defined carbohydrate surfactants bearing carbosilane, silane, polysilane and non-permethylated siloxane moieties. These compounds will serve as models in a comprehensive investigation of the structure-dependent wetting properties in aqueous solution.

In a continuation of the investigation of SiH-functionalized precursors,[8] the wetting data of the key intermediates, the slightly polar allyl glycidyl derivatives, will be discussed. This type of substance bridges the gap from the SiH-functionalized precursors to the highly polar and water-soluble carbohydrate surfactants.

2 METHODS AND MATERIALS

2.1 Methods

The ^{13}C NMR spectra were recorded on a Varian XL 300 spectrometer using $CDCl_3$ (epoxides) and deuterated dimethyl sulphoxide (DMSO) (carbohydrate derivatives) as solvents and internal standards.

Column GC experiments were carried out on a Varian 1400 chromatograph. A 0.5 m steel column ($\frac{1}{8}$-inch, 3.2 mm) packed with Chromosorb W-AW-DCMS (80–100-mesh) and modified with 10% SE 30 has been applied (temperature programme: 50→280 °C; heating rate 10 °C min^{-1}; FID).

The GC–MS coupling experiments were carried out on a Hewlett–Packard HP GC 5890/MSD 5970 combination. A 20 m glass column (diameter 0.18 mm, modified with 0.5 μm crosslinked polystyrene DB-5; temperature programme: 5 min at 35 °C, afterwards 35→270 °C, heating rate 20 °C min^{-1}; electron impact mass spectra) has been used.

The elemental analysis data were determined on a Carlo Erba analyser, model 1106.

Contact angles θ of the silicon-containing epoxides on an FER® plate (tetrafluoroethylene–hexafluoropropylene copolymer, DuPont, solid surface tension γ_{sv} 18.9 mN m^{-1} determined in previous experiments) were determined by independent measurements of the surface tension γ_{lv} (ring method) and wetting tension α (Wilhelmy method) (Eqn [1]). Each measurement was carried out at 20 °C.

$$\frac{\alpha}{\sigma} = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} = \cos\theta \qquad [1]$$

The surface tensions γ_{lv} of the liquids were measured with a Pt–Ir ring. The force values obtained were corrected according to Harkins and Jordan.[28]

The wetting experiments have been explained in detail in earlier papers.[7, 8]

In order to obtain reproducible wetting tension data the FEP® plate had to be cleaned carefully. After ultrasonication in 2-propanol the plate was immersed in a solution consisting of H_2SO_4 (39 parts), water (11 parts) and $K_2S_2O_8$ (1.5 parts) and afterwards in a strongly basic solution (3 parts 2-propanol, 1 part water, 1 part KOH).

To measure the wetting tension α the FEP® plate of defined width and thickness (1.818 cm × 0.0245 cm) was dipped stepwise (usually 0.1 cm, immersion velocity 0.1 cm min^{-1}) into the liquid with an accuracy of 0.001 cm.

The force p measured correlates with α (Eqn [2]).

$$p = ua + (-)rgdbx_e \qquad [2]$$

where

u = perimeter of the FEP® plate
r = liquid density
g = gravitational constant
d = thickness of the plate
b = width of the plate
x_e = immersion depth of the plate

After every movement of the plate we measured the force immediately and after 1 min. This time was found necessary for the system to reach an equilibrium state of wetting. By plotting the 1 min values of the force p against the immersion depth x_e, one yields by extrapolation to $x_e = 0$ the wetting tension α.

The solid/liquid interfacial tension γ_{sl} can be determined from the γ_{sv}–α relationship (see Eqn [1]). Provided the solid is non-polar, knowledge of its solid surface tension γ_{sv} makes possible the determination the Lifshitz–van der Waals portions of the surface tension[29] (γ_{lv}^{LW}) (Eqn [3]) and solid/liquid interfacial tension[30] (γ_{sl}^{LW}) (Eqn [4]) of the liquids under investigation.

$$\gamma_{lv}^{LW} = \left[\frac{\gamma_{lv}\cdot(1+\cos\theta)}{2\sqrt{\gamma_{sv}^{LW}}}\right]^2 \qquad [3]$$

$$\gamma_{sl}^{LW} = \gamma_{s}^{LW} + \gamma_{l}^{LW} - 2\sqrt{\gamma_{s}^{LW}\cdot\gamma_{l}^{LW}} \qquad [4]$$

The polar portions ($\gamma_{lv}^{+/-}$) and ($\gamma_{sl}^{+/-}$) were calculated in analogy to Fowkes' approach[31] by

$$\gamma_{lv}^{+/-} = \gamma_{lv} - \gamma_{lv}^{LW} \qquad [5]$$

$$\gamma_{sl}^{+/-} = \gamma_{sl} - \gamma_{sl}^{LW} \qquad [6]$$

2.2 Materials

The syntheses of SiH-functionalized carbosilanes, silanes, polysilanes and non-permethylated siloxanes have been already described.[8]

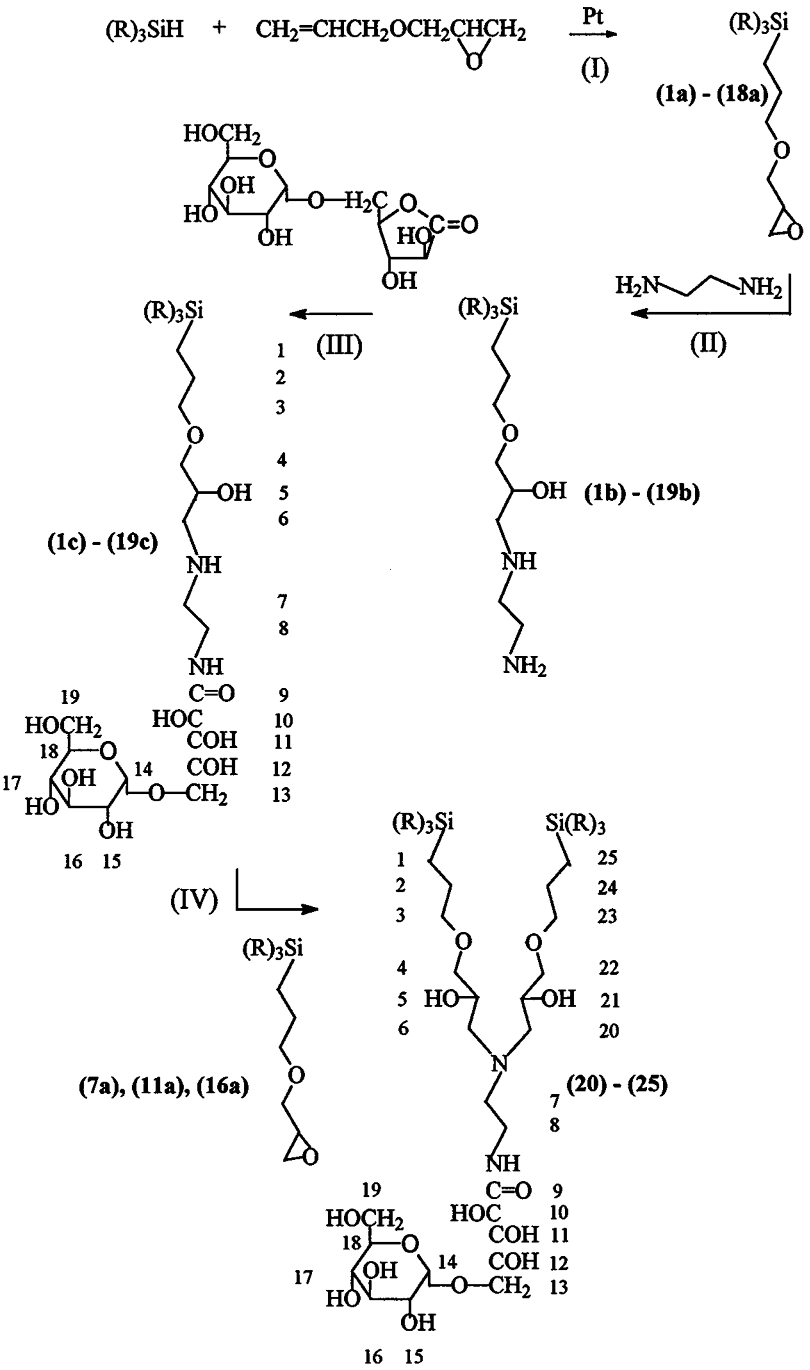
The reaction sequence hydrosilylation (I), monoalkylation of ethylenediamine (II), nucleophilic lactone ring opening (III) and optional alkylation of the remaining secondary amino function (IV) yields carbohydrate-modified derivatives bearing different hydrophobic silicon moieties (Scheme 1).

The epoxides **1a**–**12a** have been synthesized under inert conditions by platinum-catalysed (Lamoreaux catalyst[32]) hydrosilylations.[1, 13, 33] The molar ratios of the reactants were chosen to be SiH/C = C/Pt = $1{:}1.2{:}2\times10^4$ [Table 1; Scheme 1; reaction (I)]. The synthesis of compounds **13a**–**16a** and **18a** has been described elsewhere.[1] Compound **17a** was provided from internal Bayer AG sources.

Compound **19a** bearing a disilane moiety was synthesized in an azoisobutyronitrile (AIBN)-catalysed radical reaction[27] (Scheme 2). Thus, 5 g (3.8×10^{-2} mol) of pentamethyldisilane, 5.6 g (4.9×10^{-2} mol) of freshly distilled allyl glycidyl ether and 0.1 g of AIBN were mixed in a two-necked quartz bottle (50 ml) under an argon atmosphere. The temperature was raised to 120 °C for 8 h. By means of GC, a conversion of about 5% was found. Then 0.05 g of AIBN was added and the quartz bottle irradiated for 24 h with 200–300 nm light (source: mercury vapour lamp, beam guided to the bottle via glass fibres). Afterwards the mixture was reheated to 120 °C for 50 h. The conversion rose to 30%. Further AIBN additions combined with heating and UV irradiation cycles did not increase the conversion. Therefore an analogous experiment was carried out (conversion 12%), both mixtures were afterwards combined and the epoxide **19a** was isolated by distillation under reduced pressure (1 g, b.p. 126–130 °C/12 mmHg).

The epoxides **1a**–**8a**, **10a**–**11a**, **16a** and **19a** have been used for the regioselective monoalkylation of ethylenediamine yielding the corresponding silicon-modified primary–secondary diamines **1b**–**19b**. The procedure (five-fold molar excess of ethylenediamine dissolved in refluxing methanol, epoxide dropped in, reaction time 1 h) has been described earlier[1] [Scheme 1, reaction (II)].

After complete evaporation of methanol and ethylenediamine in vacuum (90 °C/1 mmHg), the viscous and pale-yellow diamines have been used without further purification for the nucleophilic lactone ring opening of glucopyranosyl



Scheme 1. Reaction sequence for synthesis of carbohydrate-modified derivatives bearing hydrophobic silicon moieties.

Table 1 Reaction conditions and product data of silicon-modified allyl glycidyl ether derivatives

No.	Silicon substituent R	Reaction time (h)	Temp. (°C)	Yield (%)	B.p. (°C/mmHg)	Density (g cm^{-3})
1a	$[(CH_3)_3SiO]_2Si(C_2H_5)$–	2	80	89	118–120/1.4	
2a	$[(CH_3)_3SiO]_2Si(C_6H_5)$–	2	110	78	141–148/1	0.971
3a	$(CH_3)_3SiOSi[(CH_3)_2]CH_2Si[(CH_3)_2]$–	2	70	82	160–164/6	0.905
4a	$(CH_3)_3SiCH_2Si[(CH_3)_2]OSi[(CH_3)_2]$–	2	100	80	120–127/1	0.897
5a	$(CH_3)_3CSi[(CH_3)_2]OSi[(CH_3)_2]$–	2	80	80	128–132/2	0.908
6a	$(CH_3)_3CCH_2CH_2SiOSi[(CH_3)_2]$–	1	100	75	122–124/0.7	
7a	$(CH_3)_3SiCH_2Si[(CH_3)_2]$–	6	120	81	115–122/2	0.897
8a	$[(CH_3)_3SiCH_2]_2Si(CH_3)$–	6	120	50	120–125/0.5	0.899
9a	$[(CH_3)_3SiCH_2]_3Si$–	6	120	36	150–156/2	
10a	$(CH_3)_3Si$–	4	50	72	112–120/30	0.893
		1	100			
11a	$(CH_3)_3CCH_2Si[(CH_3)_2]$–	5	130	67	130–135/2.8	0.893
12a	$[(CH_3)_3CCH_2]_2Si(CH_3)$–	2	110	53	142–150/2	
13a[a]	$[(CH_3)_3SiO]_2Si(CH_3)$–			85	129–132/3	0.932
14a[a]	$(CH_3)_3SiOSi[(CH_3)_2]OSi[(CH_3)_2]$–			74	120–125/2.5	0.922
15a[a]	$[(C_2H_5)_3SiO]_2Si(CH_3)$–			35	137–147/0.7	0.938
16a[a]	$(CH_3)_3SiOSi[(CH_3)_2]$–			82	130–135/7.5	0.914
17a[a]	–$Si[(CH_3)_2]OSi[(CH_3)_2]$–					0.998
18a[a]	$[(CH_3)_3SiO]_3Si$–			57	162–167/7.5	0.932
19a	$(CH_3)_3SiSi[(CH_3)_2]$–				126–130/12	0.998

[a] Synthesis described in Ref. 1.

arabinonic acid lactone. The stoichiometric reactions were carried out in refluxing methanol for 4 h and yielded quantitatively the glucopyranosyl arabinonic acid amides as pale-yellow powder [Scheme 1, reaction (III)].

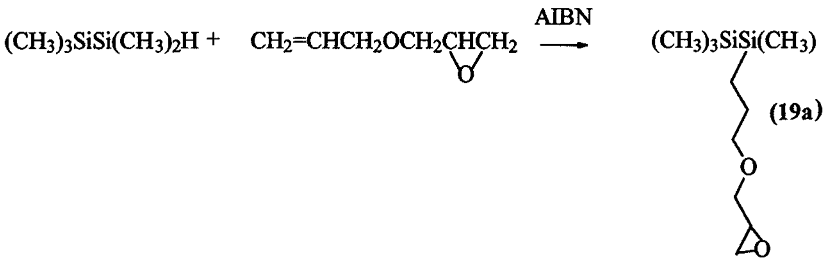
The carbohydrate derivatives **1c**–**8c**, **10c**–**11c**, **16c** and **19c** have been characterized by their ^{13}C NMR spectra (Tables 2 and 3), elemental analysis and solubility data (Table 7). The relevant data for compounds **13c**–**15c** have already been published.[1]

The carbohydrate-modified compounds **7c**, **11c** and **16c** were used as precursors for the synthesis of double-chained derivatives [Scheme 1, reaction (IV)]. Thus, the remaining secondary amino function was alkylated in a straightforward reaction with the epoxides **7a**, **11a** and **16a** yielding products bearing two independent silicon units of the same or different type.

The stoichiometric reactions were carried out in a steel autoclave at 80 °C for 8 h (solvent, methanol). The epoxide concentration was monitored by gas chromatography and its disappearance was taken as an indication of the end of the reaction. In all six cases under investigation we found complete conversion.

As these double-chained derivatives **20**–**25** have considerable solubility in all low-boiling solvents from water to n-alkanes, we were not able to precipitate and recrystallize them.

To remove all traces of methanol, we dissolved the crude products several times in diethyl ether and evaporated both solvents simultaneously. Sticky yellow powders or waxes were obtained. They were characterized by their ^{13}C NMR spectra (Table 4 and 5) and elemental



Scheme 2. Synthesis of **19e**.

Table 2 ^{13}C NMR data of compounds **1c**–**8c**, **10c**–**11c**, **16c** and **19c**

No.	Silicon substituent R	Shift (ppm)				
1c	$[(CH_3)_3SiO]_2Si(CH_2CH_3)$–	$(CH_3)_3$	CH_2	CH_3		
		1.84	7.46	6.41		
2c	$[(CH_3)_3SiO]_2Si(C_6H_5)$–	$(CH_3)_3$	SiC	*o*-Phenyl C	*m*-Phenyl C	*p*-Phenyl C
		1.86	129.95	127.98	133.24	136.87
3c	$(CH_3)_3SiOSi[(CH_3)_2]CH_2Si[(CH_3)_2]$–	$(CH_3]_3$	$[(CH_3)_2]$	CH_2	$Si[(CH_3)_2]$–	
		2.03	0.84	4.38	3.26	
4c	$(CH_3)_3SiCH_2Si[(CH_3)_2]OSi[(CH_3)_2]$–	$(CH_3)_3$	CH_2	$[(CH_3)_2]O$	$[(CH_3)_2]$–	
		1.15	6.21	3.26	0.33	
5c	$(CH_3)_3CSi[(CH_3)_2]OSi[(CH_3)_2]$–	$(CH_3)_3$	C	$[(CH_3)_2]O$	$[(CH_3)_2]$–	
		25.64	17.78	− 2.87	0.38	
6c	$(CH_3)_3CCH_2CH_2Si[(CH_3)_2]OSi[(CH_3)_2]$–	$(CH_3)_3$	C	CH_2CH_2	$[(CH_3)_2O$	$[(CH_3)_2$–
		28.67	36.77	30.63, 12.04	0.14	0.33
7c	$(CH_3)_3SiCH_2Si[(CH_3)_2]$–	$(CH_3)_3$	CH_2	$[(CH_3)_2]$–		
		1.45	2.01	− 0.58		
8c	$[(CH_3)_3SiCH_2]_2Si(CH_3)$–	$(CH_3)_3$	CH_2	CH_3		
		1.55	3.07	0.34		
10c	$(CH_3)_3Si$–	$(CH_3)_3$				
		1.65				
11c	$(CH_3)_3CCH_2Si[(CH_3)_2]$–	$(CH_3)_3$	C	CH_2	$[(CH_3)_2]$	
		32.88	30.75	32.02	− 0.94	
16c	$(CH_3)_3SiOSi[(CH_3)_2]$–	$(CH_3)_3$	$[(CH_3)_2]$			
		2.01	0.32			
19c	$(CH_3)_3SiSi(CH_3)_2$–	$(CH_3)_3$	$(CH_3)_2$–			
		− 2.04	− 4.31			

Table 3 ^{13}C NMR data of the spacer and the carbohydrate moiety of compound **11c**

C atom	1	2	3	4	5	6	7	8	9	10
Shift (ppm)	12.66	23.81	73.40	73.52	68.50	52.51	48.70	38.25	173.48	73.64
C atom	11	12	13	14	15	16	17	18	19	
Shift (ppm)	70.89	69.42	68.80	98.94	71.70	72.46	70.16	72.34	60.81	

Table 4 ^{13}C NMR data of the silicon moieties in the double-chained compounds **20**–**25** (shifts in ppm)

No.	Moiety 1	Moiety 2	$(CH_3)_3$	C	CH_2	$(CH_3)_2$
20	$(CH_3)_3SiOSi(CH_3)_2$–	$(CH_3)_3SiOSi(CH_3)_2$–	2.05			0.35
21	$(CH_3)_3SiOSi(CH_3)_2$–		2.06			0.36
		$[CH_3)_3SiCH_2Si(CH_3)_2$–	1.47		2.12	− 0.56
22	$(CH_3)_3SiOSi(CH_3)_2$–		2.06			0.36
		$(CH_3)_3CCH_2Si(CH_3)_2$–	32.85	30.74	31.98	− 0.97
23	$(CH_3)_3SiCH_2Si(CH_3)_2$–	$(CH_3)_3SiCH_2Si(CH_3)_2$–	1.44		2.08	− 0.59
24	$(CH_3)_3SiCH_2Si(CH_3)_2$–		1.42		2.09	− 0.61
		$(CH_3)_3CCH_2Si(CH_3)_2$–	32.82	30.67	31.98	− 1.01
25	$(CH_3)_3CCH_2Si(CH_3)_2$–	$(CH_3)_3CCH_2Si(CH_3)_2$–	32.84	30.71	31.98	− 0.99

Table 5 ^{13}C NMR data of the spacer and the carbohydrate moiety of compound **22**

C atom	1	2	3	4	5	6	7	8	9	10
Shift (ppm)	12.64	23.78	73.51	73.20	67.40 67.95	58.30 58.70	54.90 55.10	36.50	173.26 173.55	73.61
C atom	11	12	13	14	15	16	17	18	19	20
Shift (ppm)	70.70	69.39	68.76	98.93	71.80	72.44	70.11	72.34	60.77	58.30 58.70
C atom	21	22	23	24	25					
Shifta (ppm)	67.40 67.95	73.20	73.34	23.12	13.91					

analysis data.

The elemental analysis data of compounds **1c**–**8c**, **10c**–**11c**, **16c** and **19c** to **25** are in good agreement with the theoretical values (difference $<1\%$ for C).

3 RESULTS AND DISCUSSION

3.1 Glucopyranosyl arabinonic acid amides

It was one important aim of this investigation to provide defined Si-containing carbohydrate surfactants which deviate from the known[1, 7] permethylated siloxanyl compounds by four structural features: (1) replacement of siloxanyl moieties' 'methyl side chains' by bulkier alkyl or aryl structures; (2) partial or complete elimination of oxygen from the silicon-containing backbone; (3) substitution of silicon by carbon with maintenance of the branched structure; and (4) incorporation of a second independent non-siloxane hydrophobe.

Carbosilanes, silanes, non-permethylated siloxanes and double-chained derivatives were synthesized in analogy to the permethylated siloxanyl ones. Hydrosilylation, alkylation of ethylenediamine, lactone ring opening and the optional alkylation of the remaining secondary amino function were carried out under comparable conditions [Scheme 1, reaction (I)–(IV)].

Although Pt-catalysed hydrosilylations of polysilanes have already been claimed,[34] we failed to synthesize the epoxide via this route. Mixing of pentamethyldisilane, allyl glycidyl ether and Lamoreaux catalyst at room temperature led to a slow but constant gas evolution accompanied by the formation of higher-molecuar-weight products. A temperature increase to 45 °C led to rapid disilane decomosition. The sequence of substance addition did not alter this result. Addition of (a) Pt catalyst into the disilane/epoxide mixture, (b) epoxide/Pt catalyst mixture into the disilane or (c) epoxide into the disilane/Pt-catalyst mixture yielded the same results.

A GC–MS investigation of the complex product mixture (Table 6) showed that a broad spectrum of oligosilanes is formed. This product type has already been synthesized from $(CH_3)_3SiSi(CH_3)_2H$ by catalytic coupling (catalyst Cp_2ZrR_2) with elimination of trimethylsilane.[35] Pentamethyldisilane disappears completely, whereas considerable amounts of

Table 6 Reaction of pentamethyldisilane and allyl glycidyl ether in the presence of Lamoreaux catalyst; relative abundance of key fragments of the main products

Retention time (min)	43 $[SiCH_3]$	45 $[H_2SiCH_3]$	59 $[HSi(CH_3)_2]$	73 $[Si(CH_3)_3]$	101 $[Si_2(CH_3)_3]$	131 $[Si_2(CH_3)_5]$	173 $[Si_3(CH_3)_6{-}H]$
8.07	53	100		29			
11.59	13	21	74		100	13	
12.92	24	29	37	100	84	8	
16.06	8	13	34		100	32	3
$(CH_3)_3SiSi(CH_3)_2H$	21	18	10	100	3	8 (M^+)	

allyl glycidyl ether remain in the mixture. Only traces of the desired hydrosilylation product are found.

Alternatively we carried out AIBN-catalysed radical hydrosilylation reactions[27] (Scheme 2). In long-run, low-yield procedures under thermal and UV-light initiation conditions we were able to synthesize a sufficient amount of the disilane derivative. It was found empirically that alternating thermal and UV initiation conditions were the only way to obtain conversions above 20%. Thermal treatments of UV initiation alone gave maximum conversions between 5 and 10%. It had been a common feature of all reactions that, from a certain point onwards, the conversion remained constant. Neither additional initiator nor thermal or UV treatments improved the yield. Experiments with dibenzoyl proxide failed completely. The reason for this extreme inhibition of the radical hydrosilylation and the sensitivity towards the initiator type is not well understood but could be due to a decreased stability of the epoxide under reaction conditions.

Fortunately, the well-known base-catalysed Si-Si bond cleavage[36] did not take place during the ethylenediamine alkylation so that, from this point on, the well-established procedure could be applied.

The solubility of the surfactants in organic liquids depends on the hydrophobe structure (Table 7). The substitution of methyl groups in **13c** by one **1c** or six ethyl groups **15c** considerably increases the organic solubility. On the other hand, a phenyl substitution **2c** does not have the same effect. Even the expected improved solubility in aromatic solvents was not found. Probably this contradictory solubility behaviour reflects the fundamental energy differences between ethyl and phenyl substituents, which will be discussed in the next section.

As expected, more branched hydrocarbon substituents on silicon (**10c**, methyl→**11c**, neopentyl) improve the organic solubility.

Minor but significant differences were found for isomeric siloxanes **16c**, polysilanes **19c**, carbosilanes **7c** and silanes **11c**. Probably due to their strengthened hydrocarbon character, compounds **7c** and **11c** were more soluble in the organic solvents.

In order to improve the organic solubility, we incorporated two independent silicon hydrophobes. Figure 2 demonstrates the consequences of identical (siloxane/siloxane, **20**) and different (siloxane/carbosilane, **21**; siloxane/neopentylsilane, **22**) silicon hydrophobes on the ^{13}C NMR shift pattern. In mixed structures two sets of signal for the methylene units adjacent to silicon emerge.

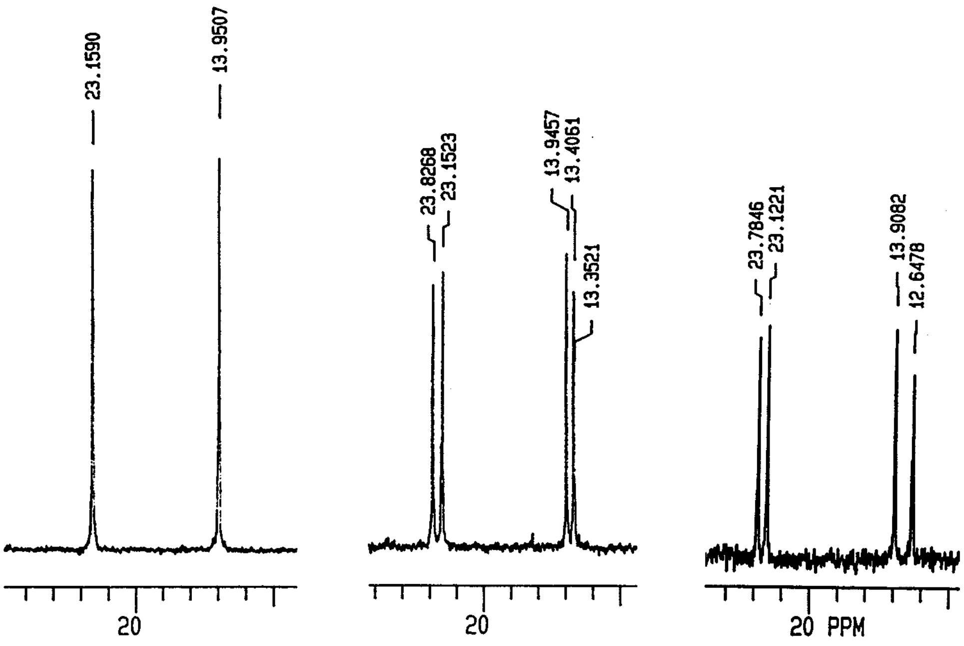
Although it is sufficiently soluble in water, test substance **24** can be dissolved in almost all weak polar organic media. The solubility profile of such structures comes close to that of hydrocarbon-based double-chained lipids.

We have already discussed the wetting behaviour of SiH-functionalized liquid precursors[8] and aqueous solutions of carbohydrate-modified siloxane surfactants[7] on perfluorinated surfaces. Unlike surface-active oligo-oxyethylene derivatives of the Silwet L77 type $[(CH_3)_3SiO]_2\,Si(CH_3)CH_2\,CH_2\,CH_2\,(OCH_2CH_2)_{7.5}\,OCH_3]$, these carbohydrate species are viscous syrups, waxes or powders. Wetting experiments with pure carbohydrate derivatives are impos-

Table 7 Solubility[a] of selected surfactants in solvents of different polarity

No.	NMP	NOP	Hallcomid M8–10	Xylene	1,2,3-Trimethylbenzene	Isophorone	Octyl acetate	Rape-oil methyl ester	Paraffin oil
1c	+	+	+	+	+	−	−	−	−
2c	+	+	+	±	−	−	−	−	−
7c	+	+	−	−	−	−	−	−	−
10c	+	−	−	−	−	−	−	−	−
11c	+	+	−	−	−	−	−	−	−
13c	+	+	+	−	−	−	−	−	−
15c	+	+	+	+	+	+	+	+	−
16c	+	±	−	−	−	−	−	−	−
19c	+	−	−	−	−	−	−	−	−
24	+	+	+	+	+	+	+	+	−

[a] Solubility of 7.15% surfactant in the solvent at room temperature: +, soluble; −, insoluble; ±, turbid; NMP, *N*-methylpyrrolidone; NOP, *N*-octylpyrrolidone; Hallcomid M8–10, C_8–C_{10} carboxylic acid amide.



(20) **(21)** **(22)**

Figure 2 $\equiv Si\underline{C}H_2\underline{C}H_2CH_2O$– regions of the ^{13}C NMR spectra of compounds **20**, **21** and **22**.

sible. On the other hand, the wetting and spreading performance of Silwet L77 changes dramatically from bulk to aqueous solution. Considerable surface tension (γ_{lv}) and solid/liqid interfacial tension (γ_{sl}) reductions[8] are accompanied by increased spreading rates.[37–39] The presence of water is essential for the superspreading property.

The polar but liquid epoxides under investigation could be understood as intermediates. They bridge the gap from the unfunctionalized, low-viscosity precursors to the aqueous carbohydrate surfactant solutions which will be discussed in a separate paper.

In a few cases epoxides and aqueous surfactant solutions[8] can already be compared (Figs 3 and 4).

With the exception of the tetrasiloxyanyl epoxide **18a** and its carbohydrate derivative, in all cases the siloxanyl epoxides have higher surface tensions and solid/liquid interfacial tensions on FEP®. The forces in dense siloxane surfactant monolayers,[7] precursor liquids[8] and epoxides at the liquid/vapour interface are predominantly of the Lifshitz–van der Waals type, whereas for water donor–acceptor contributions dominate (21 mN m^{-1} Lifshitz–van der Waals portion, 51 mN m^{-1} donor–acceptor portion[40]). Therefore we assume that (depending on the structure) the extent of intermolecular interactions of both the Lifshitz–van der Waals and/or the donor–acceptor type can change if the molecules directly exposed to interfaces are adjacent to molecules of the same chemical and energy composition instead of water.

The trends within the epoxide group are due to the impact of different silicon hydrophobes. Deviations from the energetically successful concept of a ‘permethylated siloxane backbone’ **13a** yield increased surface tensions and solid/

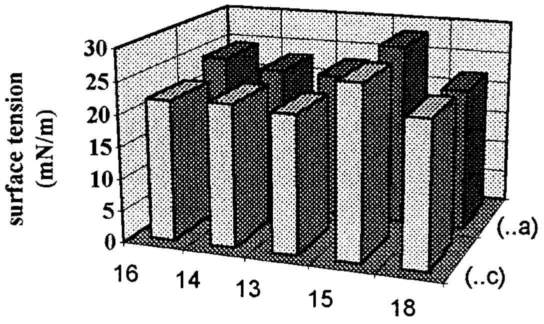


Figure 3 Surface tension of selected siloxanyl epoxides (. . **a**) and of aqueous solutions of the corresponding carbohydrate derivatives (. . **c**). Solution data are taken from Ref. 8; for general molecular structure, see Tables 1 (. . **a**) and 2 (. . **c**).

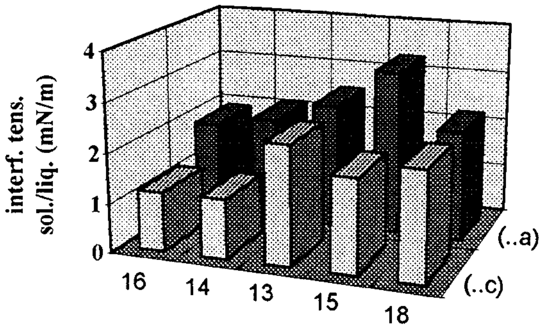


Figure 4 Solid/liquid interfacial tension on FEP® of selected siloxanyl epoxides (**. . a**) and of aqueous solutions of the corresponding carbohydrate derivatives (**. . c**). Solution data are taken from Ref. 8; for general molecule structure, see Tables 1 (**. . a**) and 2 (**. . c**).

liquid interfacial tensions. The addition of six $-CH_2-$ units in derivative **15a** strongly increases Lifshitz–van der Walls contributions. A phenyl substitution of the trisiloxane structure **2a** predominantly strengthens donor–acceptor portions (Fig 5 and 6).

Alternatively to methylene units or aromatic rings, the t-butyl-substituted compound **5a** bears additional methyl groups. Comparison with substance **16a** shows that these additional methyl groups generate a moderate surface tension increase (Lifshitz–van der Waals portion, γ_{lv}^{LW}). A significant increase in the Lifshitz–van de Waals portion of the solid/liquid interfacial energy γ_{sl}^{LW} is not observed. Clearly, 'branching' methyl groups increase interfacial energies less efficiently than 'chain-extending' methylene moieties.

As one might argue that the methyl groups in

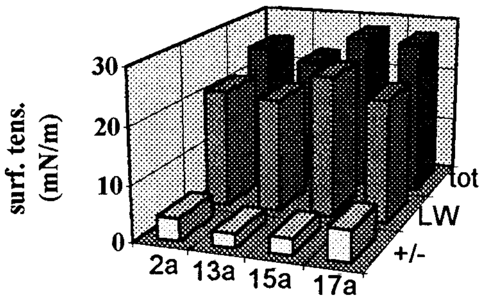


Figure 5 Surface tension of selected siloxanyl epoxides: $+/-$, donor–acceptor contributions; LW, Lifshitz–van der Waals contributions; tot, total.

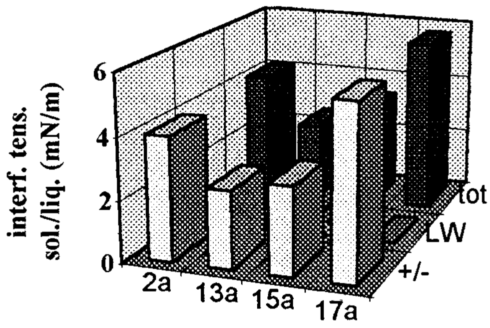


Figure 6 Solid/liquid interfacial tension on FEP® of selected siloxanyl epoxides: $+/-$, donor-acceptor contributions; LW, Lifshitz–van der Waals contributions; tot, total.

Table 8 Wetting data of selected epoxides and pure Silwet L77 on FEP®

No.	γ_{lv} (mN m^{-1})	γ_{lv}^{LW} (mN m^{-1})	$\gamma_{lv}^{+/-}$ (mN m^{-1})	γ_{sl} (mN m^{-1})	γ_{sl}^{LW} (mN m^{-1})	$\gamma_{sl}^{+/-}$ (mN m^{-1})	α (mN m^{-1})	cos θ	θ (grd)
2a	25.0	21.0	4.0	4.1	0.1	4.0	14.8	0.593	53.6
3a	24.7	22.7	2.0	2.2	0.15	2.05	16.7	0.677	47.4
4a	25.8	24.1	1.7	2.0	0.3	1.7	16.9	0.655	49.3
5a	25.7	23.8	1.9	2.2	0.3	1.9	16.7	0.652	49.5
7a	25.1	23.1	2.0	2.2	0.2	2.0	16.7	0.665	48.3
8a	25.3	22.9	2.4	2.6	0.2	2.4	16.3	0.643	50.0
10a	26.7	23.5	3.2	3.4	0.25	3.15	15.5	0.581	54.5
11a	25.4	23.6	1.8	2.0	0.3	1.7	16.9	0.664	48.4
13a	22.8	20.3	2.5	2.5	0.0	2.5	16.4	0.718	44.1
14a	23.0	21.0	2.0	2.1	0.1	2.0	16.8	0.731	43.0
15a	28.1	25.2	2.9	3.3	0.45	2.85	15.6	0.555	56.3
16a	24.4	22.7	1.7	1.9	0.2	1.7	17.0	0.697	45.8
17a	27.5	21.9	5.6	5.7	0.1	5.6	13.2	0.479	61.4
18a	22.0	19.8	2.2	2.2	0.0	2.2	16.7	0.758	40.7
Silwet	24.6	20.8	3.8	2.7	0.0	2.7	15.1	0.614	52.1

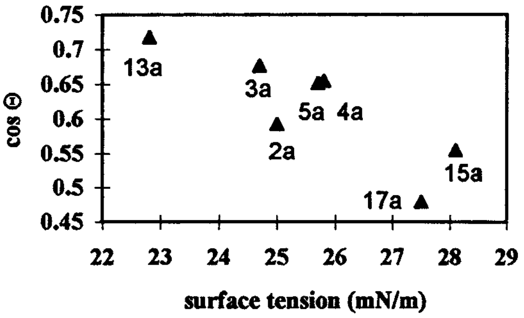


Figure 7 Surface tensions and contact angles (cos θ) of selected epoxides.

5a are attached to carbon and the methylene units in **15a** to silicon, we synthesized a series of analogous siloxanes **16a**, carbosilanes **7a** and neopentyl-substituted silanes **11a**. An inspection of the data sets of these three compounds immediately discloses that the last of these behaves in a less polar manner and forces of the Lifshitz–van der Waals type are pronounced. The property profile of this silane derivative (weakly-polar and highly energetic) is similar to that of hydrocarbons.

Nevertheless the considerable ‘background polarity’ raises the question of the role of the epoxide moiety. The substitution of a methyl group in **16a** by a second allyl glycidyl function yields the bifunctional siloxane **17a**. In contrast to the role of methylene units discussed above, the allyl glycidyl moiety increases the donor–acceptor contributions selectively. The extent of the increase is surprising, as Silwet L77 in bulk (7.5 ethylene oxide units; Table 8) is less polar and the first two disaccharide units attached to one trisiloxane block cause a comparable combination of forces in aqueous solution (compound **11** in Ref. 7).

The most interesting aspect of compound **17a** arises from a comparison with substance **15a**, as the proportions of force types in them differ fundamentally. Despite its higher surface tension, substance **15a** wets the perfluorinated material better than the more polar molecule **17a** does. This is due to a lower γ_{sl} which in this particular case compensates for the surface tension effect. On the one hand, the donor–acceptor portions of the surface tension ($\gamma_{lv}^{+/-}$) are completely transformed into equivalent $\gamma_{sl}^{+/-}$ contributions. On the other hand, the γ_{lv}^{LW-} contributions are compensated and do not create significant γ_{sl}^{LW} portions (Figs 5 and 6). The non-polar, perfluorinated material interacts selectively and a surface-tension-independent contact angle is the consequence (Fig. 7).

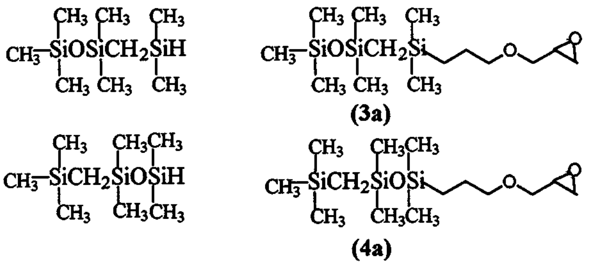


Figure 8 Structures of epoxy-modified compounds **3a** and **4a**.

In a previous paper[8] we were able to show that in a comparison between $(CH_3)_3Si\underline{\mathbf{O}}\text{-}Si[(CH_3)_2]CH_2Si(CH_3)_2\underline{\mathbf{H}}$ and $\underline{\mathbf{H}}(CH_3)_2Si\underline{\mathbf{O}}Si[(CH_3)_2]CH_2Si(CH_3)_3$ the latter reresents a low-energy penta-alkyl-substituted disiloxane. The former molecule was found to be a higher-energy hexa-alkyl derivative.

After epoxide functionalization this character changes (Fig. 8). Provided that for energetic reasons the epoxide functions are oriented to the interior of the liquid, the data set for compound **3a** describes a siloxane (low-energy, polar) and that for substance **4a** a carbosilane (higher-energy, less-polar).

These data also emphasize the importance of the position of single (here, oxygen) atoms in molecules at interfaces. Probably there is a distance-decay for donor–acceptor forces at interfaces which could be monitored by systematic derivatization. Unfortunately the epoxide-related ‘background polarity’ masks this effect for the substances under investigation.

In a separate paper we will describe this distance-decay for aqueous surfactant solutions.

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REFERENCES

1. R. Wagner, L. Richter, R. Wersig, G. Schmaucks, B. Weiland, J. Weissmüller and J. Reiners, *Appl. Organometal. Chem.* **10**, 421 (1996).
2. R. Wagner, L. Richter, B. Weiland, J. Weissmüller and J. Reiners, *Appl. Organometal. Chem.* **10**, 437 (1996).

3. R. Wagner, L. Richter, B. Weiland, J. Weissmüller, J. Reiners and W. Krämer, *Appl. Organometal. Chem.* **11**, 523 (1997).
4. R. Wagner, L. Richter, R. Wersig, G. Schmaucks, B. Weiland, A. Hennig, A. Jänicke, J. Reiners, J. Weissmüller, W. Krämer and W. Wirth, DE-OS 4318536 (1994).
5. R. Wagner, L. Richter, R. Wersig, G. Schmaucks, B. Weiland, A. Hennig, A. Jänicke, J. Reiners, J. Weissmüller, W. Krämer and W. Wirth, DE-OS 4318537 (1994).
6. R. Wagner, L. Richter, R. Wersig, G. Schmaucks, B. Weiland, A. Hennig, A. Jänicke, J. Reiners, J. Weissmüller, W. Krämer and W. Wirth, DE-OS 4318539 (1994).
7. R. Wagner, L. Richter, J. Reiners, J. Weissmüller, K.-D. Klein, D. Schaefer and S. Stadtmüller, *Appl. Organometal. Chem.* **11**, 617 (1997).
8. R. Wagner, L. Richter, Y. Wu, J. Reiners, J. Weissmüller, E. Hengge, A. Kleewein and K. Hassler, Part V of this series, *Appl. Organometal Chem.* **11**, 645 (1997).
9. R. Menescal and R. West, *Macromolecules* **24**, 329 (1991).
10. T. Fujisaka and R. West, *Organometal Chem.* **449**, 105 (1993).
11. K. Oka, N. Fujiue, S. Nakanishi, T. Takata, T. Dohmaru, C.-H. Yuan and R. West, *Chem. Lett.* 875 (1995).
12. G. S. Furguson, M. K. Chaudhury, H. A. Biebuyck and G. M. Whitesides, *Macromolecules* **26**, 5870 (1993).
13. M. J. Owen, British Patent 1520421.
14. A. L. R. Colas, F. A. D. Renauld and G. C. Sawacki, US Patent 5026891.
15. G. C. Kinstedt, US Patent 4005025 (1977).
16. D. C. Heckert and D. M. Watt, US Patent 4005028 (1977).
17. D. C. Heckert and D. M. Watt, US Patent 4005030 (1977).
18. D. C. Heckert and D. M. Watt, US Patent 4006176 (1977).
19. K.-D. Klein, W. Knott, G. Koerner and M. Krakenberg, DE-OS 4330059 (1994).
20. K.-D. Klein, W. Knott, and G. Koerner, Silicone surfactants—development of hydrolytically stable wetting agents. In: Auner, N. and Weis, J. (eds), *Organosilicon Chemistry II, From Molecules to Materials*, VCH, Weinheim, 1996, pp. 613–618.
21. H. Yoshida, R. Kani, S. Hayase and K. Horie, *J. Phys. Chem.* **97**, 5370 (1993).
22. R. Kani, H. Yoshida, Y. Nakano, S. Murai, Y. Mori, Y. Kawata and S. Hayase, *Langmuir* **9**, 3045 (1993).
23. T. Seki, T. Tamaki and K. Ueno, *Macromolecules* **25**, 3825 (1992).
24. K. Oka, N. Fujiue, T. Dohmaru, S. Nakanishi, T. Takata, C.-H. Yuan and R. West, *XIth International Symposium on Organosilicon Chemistry*, Montpellier 1996, Book of Abstracts, PA 73.
25. N. Yamamoto, M. Yonaeyama, Y. Ogawa, M. Ozawa, H. Iwano and K. Ashigara, DE-OS 2215382 (1972).
26. A. Miyamoto, H. Matsukawa, S. Fujimiya, N. Yamamoto and K. Ashigara, DE-OS 2512285 (1975).
27. H. Maki, S. Saeki, I. Ikeda and S. Komori, *J. Am. Oil Chem. Soc.* **46**, 635 (1969).
28. W. D. Harkins and H. F. Jordan, *J. Am. Chem. Soc.* **52**, 1751 (1930).
29. G. Czichocki, B. Gilsenbach, M. Olschewski and L. Richter, *Plaste Kautschuk* **34**, 445 (1987).
30. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.* **13**, 1741 (1969).
31. F. M. Fowkes, *Ind. Eng. Chem.* **56**, 40 (1964).
32. H. F. Lamoreaux, US Patent 3220972.
33. R. Wagner, L. Richter and A. Jänicke, DE-OS 4437886 (1996).
34. D. Seyferth and Y.-F. Yu, US Patent 4639501 (1987).
35. E. Hengge, New ways to polysilanes—starting compounds for new silicon materials. In: *Organosilicon Chemistry, From Molecules to Materials*, Auner, N. and Weis, J. (eds), VCH, Weinheim, 1994, pp. 275–283.
36. V. Bazant, V. Chvalovsky and J. Rathousky, *Organosilicon Compounds 1*, Czechoslovak Academy of Sciences, Prague, 1965, pp. 159–162.
37. F. Tiberg and A.-M. Cazabat, *Langmuir* **10**, 2301 (1994).
38. F. Tiberg and A.-M. Cazabat, *Europhys. Lett.* **25**, 205 (1944).
39. S. Zhu, W. G. Miller, L. E. Scriven and H. T. Davis, *Colloids Surfaces* **90**, 63 (1994).
40. C. J. van Oss, M. K. Chaudhury and R. J. Good, *Chem. Rev.* **88**, 927 (1988).