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Silicon-Modified Carbohydrate Surfactants II: Siloxanyl Moieties Containing Branched Structures

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Branched siloxanyl-modified carbohydrate surfactants have been synthesized by coupling mono-, di- and poly-functional siloxanes to carbohydrate units either via a branched spacer or by attaching a separate modifying element to a straight-chained structure. Hydrophilic as well as extremely hydrophobic elements have been incorporated successfully. Siloxanyl-modified carbohydrates bearing a secondary amino function were alkylated in regioselective reactions by different epoxides ranging from glycidol- to siloxanyl-modified allyl glycidyl ether derivatives. Alternatively, carbohydrate-modified piperazinyl structures yielded cyclic subunits after alkylation. Structures bearing two identical hydrophilic groups are accessible by alkylation of carbohydrate-modified bisamides. The derivatives synthesized were characterized by means of GC, NMR and elemental analysis.

Keywords: siloxanes; surfactant; carbohydrate; amino; regioselective

INTRODUCTION

In conventional non-ionic silicone surfactants[1] the siloxanyl and polyalkoxy units are connected by a short spacer which has no distinct influence on the physicochemical properties. Few attempts have been made so far to modify the surfactant properties by a careful choice of spacer or even the introduction of a separate modifying element. For siloxanyl-modified sulphates a C_6-spacer was found to give the best wetting results.[2] It was shown recently that the incorporation of the polycyclic dicyclopentadienyl unit shifts the properties of a silicone surfactant more to the hydrocarbon side (increased surface tension and intermolecular interactions) than an equivalent straight-chained hydrocarbon unit.[3] The synthesis of cationic silicone surfactants bearing either a separate dicyclopentadienyl or even a second siloxanyl unit has also been reported.[4] Both structures are similar to the well-known double-chained lipids, the membrane building material in nature.[5]

In the first paper of our series[6] we discussed the synthesis and properties of siloxanyl-modified glycosides and polyhydroxylated amides. Whereas defined glycosides had to be prepared via a low-yield multistep sequence, the amides were accessible in almost quantitative yields. It was found that only glycosides of disaccharides possess an acceptable solubility in water. The solubility of amides of smaller carbohydrates can be improved substantially by a hydrophilic spacer bearing ether, hydroxy and secondary amino functions.

These secondary amino functions should allow the incorporation of different modifying elements in quantitative and regioselective reactions, even in the presence of a multitude of hydroxyl groups. Hydrocarbon-based polyhydroxylated amines have already been reacted with acid chlorides,[7] acid anhydrides,[8] isocyanates[9] and epoxides.[10] It is the purpose of this paper to show how the properties of a given surfactant molecule can be adjusted by the choice of a modifying element ranging from a hydrophilic polyhydroxylated unit to an extremely hydrophobic permethylated one.

METHODS AND MATERIALS

Methods

The ^{13}C-NMR spectra were recorded on a Varian XL300 spectrometer using DMSO as solvent and internal standard. Column GC experiments were carried out on a 0.5 m steel column packed with an SE 30 modified support. The elemental analysis data were determined on a Carlo Erba analyser, model 1106.

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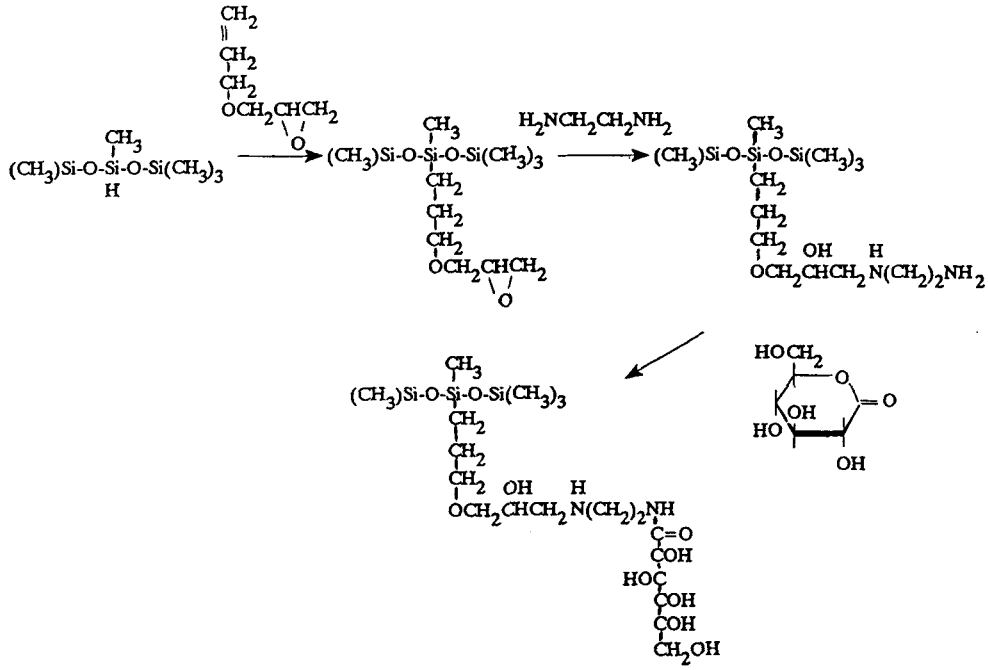


Scheme 1

Materials

Siloxanyl-modified tertiary amines

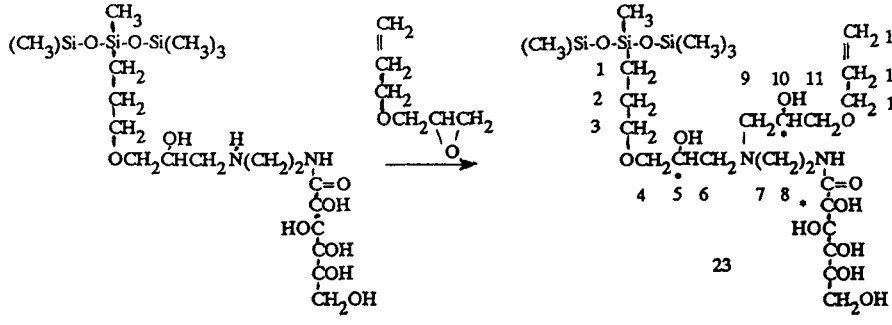
Amides bering a carbohydrate and a siloxanyl unit as well as a secondary amino function have been described in detail in part I of this series.[6] Thus, allyl glycidyl ether was hydrosilylated, the resulting epoxy siloxanes were reacted with short-chained diamines and, in a final reaction step, lactone rings were opened by a regioselective attack of the primary amino function (Scheme 1).

Due to our extensive experiences with epoxides and the availability of derivatives of graded hydrophobicity, we decided to use this group systematically for the alkylation (Eqn [1]).

The epoxides and siloxanyl-modified amines listed in Figs 1 and 2, respectively, were used.

The alkylations were carried out in a steel autoclave at 100 °C. Methanol served as solvent. The conversion of the epoxide was controlled by means of GC. In general the reactions were completed after 6 h. In a few cases an extension for 2 h was necessary (Table 1).

After the end of the reaction the solvent was removed under reduced pressure (max. 60 °C at 1 mmHg) and the remaining solid or wax-like material precipitated or was dissolved in diethyl ether or n-pentane. Precipitates were washed several times in the appropriate solvent; hydrocarbon-soluble substances isolated without further purification steps.



[1]

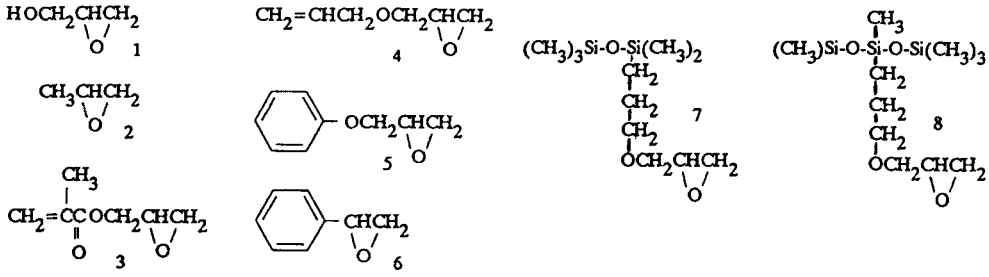


Figure 1 Structures of the epoxides.

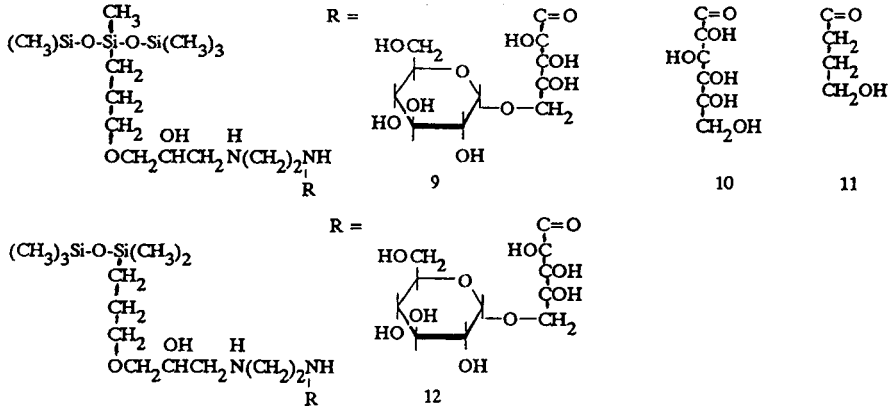


Figure 2 Structures of the secondary amines.

The substances were characterized by means of ^{13}C NMR spectroscopy and elemental analysis. (Tables 2 and 3).

Alkylation of hydrocarbon-based secondary amines

As an alternative to the strategy described above, in an initial step lactones [glucopyranosyl arabinonic acid lactone (**35**), D-gluconic acid δ-lactone (**36**), γ-butyrolactone (**37**)] were reacted regioselectively with the primary amino function(s) of primary–secondary polyamines [2-piperazin-1-ylethylamine (**38**), *N*-(2-aminoethyl)ethanolamine (**39**), diethylenetriamine (**40**), dipropylenetriamine (**41**), triethylenetetramine (**42**)] (Eqns [2], [3] and [4]).

With the exception of the γ-hydroxybutyramide species (80 °C, steel autoclave) these aminoamides were synthesized in refluxing methanol. According to GC data the polyamines disappeared quantitatively after 6 h. The products were precipitated and washed in diethyl ether and n-pentane, dried in vacuum and characterized by their ^{13}C NMR spectra (Tables 4 and 5).

In a second reaction the 1,1,1,3,5,5,5-heptamethyl-

Table 1 Alkylation of different carbohydrate-modified secondary amines by epoxides

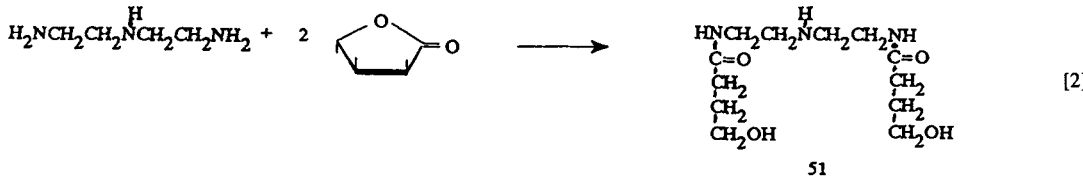
Product	Amine	Epoxide
13	**9**	**1**
14	**9**	**3**
15	**9**	**4**
16	**9**	**5**
17	**9**	**6**
18	**9**	**7**
19	**9**	**8**
20	**10**	**1**
21	**10**	**2**
22	**10**	**3**
23	**10**	**4**
24	**10**	**5**
25	**10**	**6**
26	**10**	**8**
27	**11**	**1**
28	**11**	**2**
29	**11**	**3**
30	**11**	**4**
31	**11**	**5**
32	**11**	**6**
33	**11**	**8**
34	**12**	**7**

Table 2 ^{13}C NMR data (ppm) of selected modified siloxanyl compounds (without carbohydrate signals, for their elucidation see Table 5 or Part I[6])

C atom	**15**	**19**	**24**	**25**	**27**	**28**	**34**
1	13.22	13.25	13.23	13.26	13.24	13.20	13.95
2	22.93	22.96	22.96	22.98	22.95	22.90	23.16
3	73.04	73.13	73.11	73.09	73.10	73.01	73.26
4	73.17	73.13	73.17	73.20	73.25	73.46	73.26
5	67.56	67.18/67.25/ 68.06/68.33	67.30	67.50	67.51/67.90	67.99/68.59	67.38/67.46/ 67.99/68.06
6	58.36/58.44	58.66/58.76/59.14	58.40	58.50	58.40/58.58	59.10	58.49/59.05/ 59.10
7	54.80/55.00	54.95/55.30	54.80/55.00	54.50	54.83/55.07	54.77/55.13	54.83/55.13
8	36.70	36.40	36.60	36.70	36.93/37.04	36.87/37.06	36.78
9	58.88		58.70	59.10	58.69/58.97	58.65	
10	67.98		67.56	66.10	69.23/69.59	63.26/63.89	
11	72.82		70.45	143.90/144.10	64.21/64.42	20.83/21.11	
12	71.33		158.81	125.99			
13	135.41		114.51	127.93			
14	116.22		129.42	126.90			
15			120.38				

Table 3 Elemental analysis data of selected compounds

	C (%)		H (%)		N (%)	
No.	(calc.)	(found)	(calc.)	(found)	(calc.)	(found)
14	46.70	46.56	8.25	8.37	3.30	3.17
19	44.91	44.50	8.63	9.10	2.69	2.33
23	47.09	46.86	8.86	9.01	4.07	3.79
24	49.72	49.34	8.42	8.52	3.86	3.71
27	47.48	47.12	9.53	9.70	5.04	4.75



[2]

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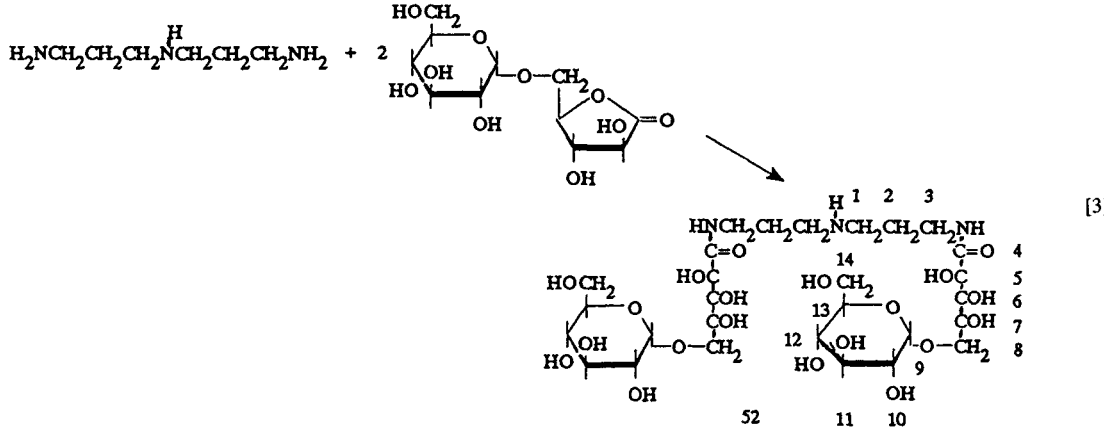

[3]

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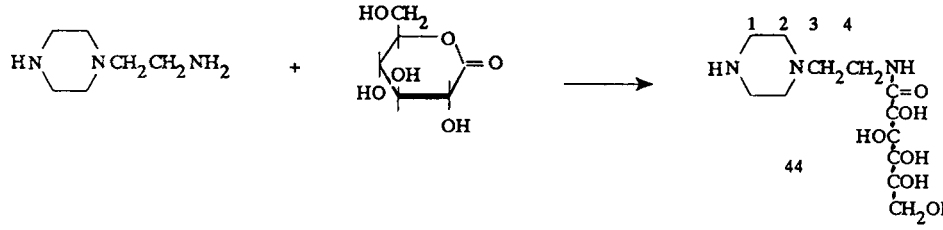


[4]

Table 4 Secondary amino functions containing hydroxylated amides

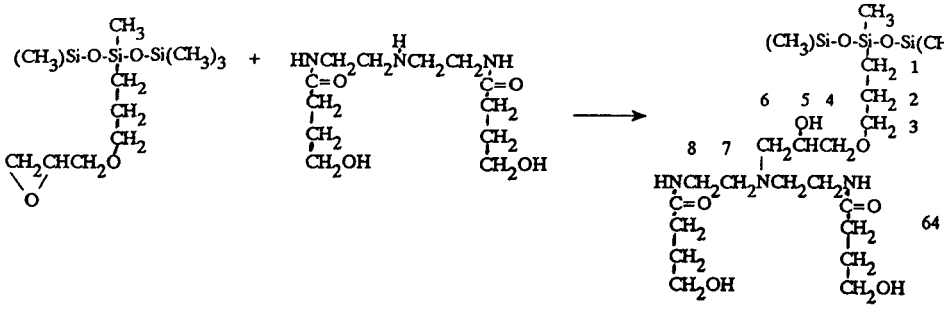
Product	Amine	Lactone	Product	Amine	Lactone
43	**38**	**35**	**49**	**40**	**35**
44	**38**	**36**	**50**	**40**	**36**
45	**38**	**37**	**51**	**40**	**37**
46	**39**	**35**	**52**	**41**	**35**
47	**39**	**36**	**53**	**41**	**36**
48	**39**	**37**	**54**	**42**	**35**
			55	**42**	**36**

trisiloxanyl-substituted allyl glycidyl ether ($MD^{Ep}M$) alkylated the remaining secondary amino function. For quantitative conversions (the epoxide content was followed by means of GC) 6–8 h at 100 °C was found to be sufficient. All reactions were carried out in a steel autoclave using methanol as solvent (Table 6; Eqns [5], [6] and [7]).

After the end of the reaction the solvent was removed under reduced pressure and the products precipitated and washed or dissolved (a few γ-hydroxybutyramide derivatives) in n-pentane. After drying in vacuum the products were characterized by

Table 5 ^{13}C NMR data (ppm) of selected hydrocarbon-based aminoamides

C atom	**44**	**46**	**47**	**50**	**51**	**52**	**53**	**55**
1	45.23	59.94	60.14	48.00	48.32	46.53	46.68	48.17
2	53.85	50.98	51.13	38.07	38.71	28.89	28.99	48.11
3	57.31	48.22	48.19	172.62	172.45	36.51	36.71	37.93
4	35.14	37.95	38.06	73.64	32.20	173.21	172.34	172.57
5	171.35	173.51	172.47	70.14	28.64	73.52	73.51	73.45
6	73.38	73.48	73.39	71.46	60.39	70.69	70.12	70.05
7	69.95	70.77	70.03	72.19		69.36	71.44	71.33
8	71.31	69.26	71.30	63.37		68.77	72.31	71.98
9	71.90	68.63	71.88			98.81	63.29	63.22
10	63.27	98.79	63.23			71.64		
11		71.62				72.36		
12		72.32				70.11		
13		70.00				72.20		
14		72.21				60.75		
15		60.66						



[5]

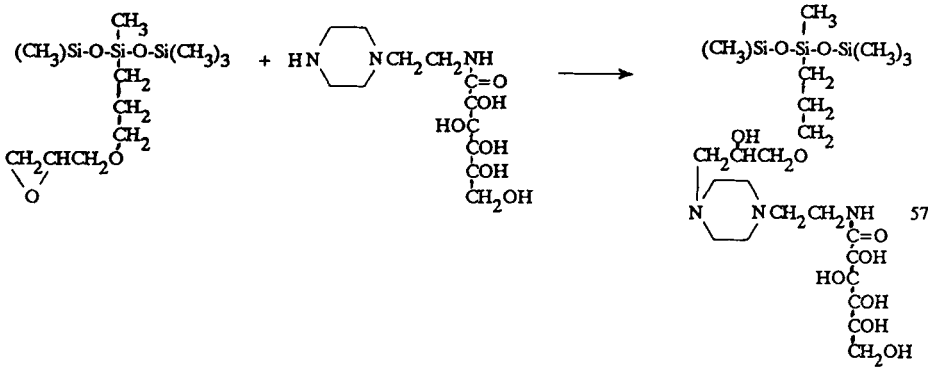
Table 6 Alkylations of different aminoamides by $MD^{Ep}M$

Product	Amine	Product	Amine	Product	Amine
56	**43**	**61**	**48**	**66**	**53**
57	**44**	**62**	**49**	**67**	**54**
58	**45**	**63**	**50**	**68**	**55**
59	**46**	**64**	**51**		
60	**47**	**65**	**52**		

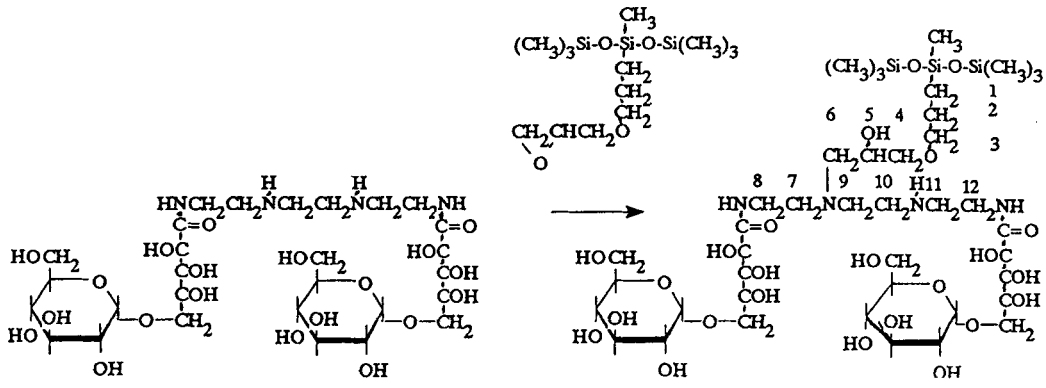
their ^{13}C NMR spectra and elemental analysis data (Tables 7 and 8).

Alkylation of amine mixtures by polymeric epoxysiloxanes

The strategy described above was also applied to epoxy functions containing polysiloxanes. The gluconamide derivative of 2-piperazin-1-ylethyl-



[6]



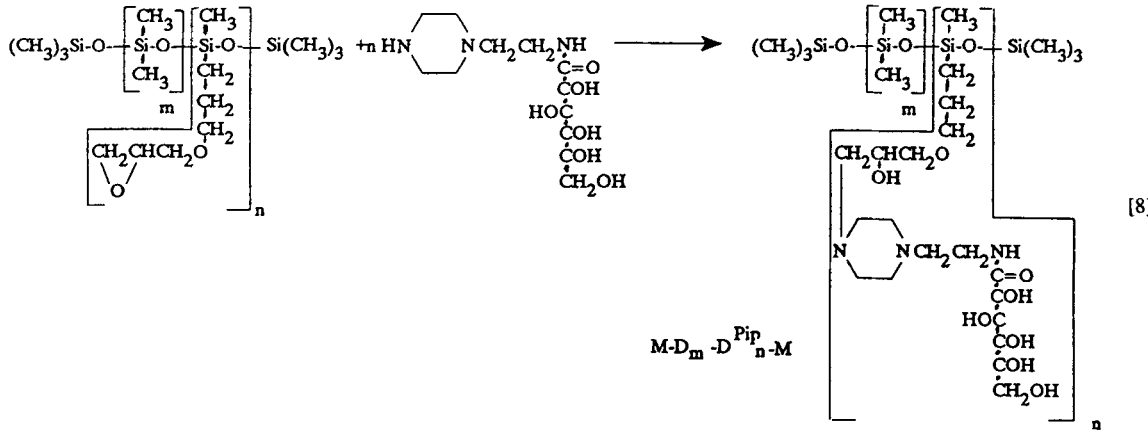
[7]

Table 7 ^{13}C NMR data (ppm) of selected siloxanyl-modified aminoamides (without carbohydrate signals; no significant shift from the data given in Table 5)

C atom	**56**	**57**	**60**	**62**	**63**	**64**	**66**	**68**
1	13.16	13.17	13.25	13.12	13.86	13.20	13.24	13.23
2	22.85	22.88	22.97	22.84	23.05	22.94	22.98	22.95
3	72.90	72.91	73.10	73.06	73.09	73.10	73.10	73.29
4	73.50	73.55	73.22	73.30	73.48	73.16	73.46	73.56
5	66.99	67.01	67.81/67.77	67.80	67.70/67.79	67.67	67.76	67.80/67.85
6	61.41	61.43	58.42	57.90	57.70	58.11	57.54	57.85
7	52.75	52.78	54.47	53.90	53.81	54.26	52.03	52.78
8	53.36	53.44	36.78	36.70	36.57	36.99	26.76	54.38/54.55
9	56.74	56.89	57.24				36.96	36.50/36.60
10	35.48	35.58	59.22					48.77
11								48.69
12								37.81

Table 8 Elemental analysis data of selected compounds

Compound	C (%)		H (%)		N (%)	
	(calc.)	(found)	(calc.)	(found)	(calc.)	(found)
56	46.45	46.10	8.39	8.59	5.42	5.10
57	46.65	45.93	8.86	8.71	6.53	6.10
59	44.80	44.46	8.27	8.32	3.73	3.41
60	44.66	44.44	8.73	8.95	4.53	4.45
63	44.19	43.72	7.65	8.06	3.96	3.98



[8]

Table 9 Carbohydrate-modified polysiloxanes of the type $MD_mD^{Pip}_nM$

Compound	*m*	*n*
69	0	10
70	2	2
71	20	20
72	11	7

Table 10 Carbohydrate-modified polysiloxanes of the type $M^{Pip}D_mM^{Pip}$

Compound	*m*	Solvent
73	15	Ethanol
74	22	Isopropanol

amine (**44**) was reacted with different polysiloxanes (Eqn [8]; Tables 9 and 10).

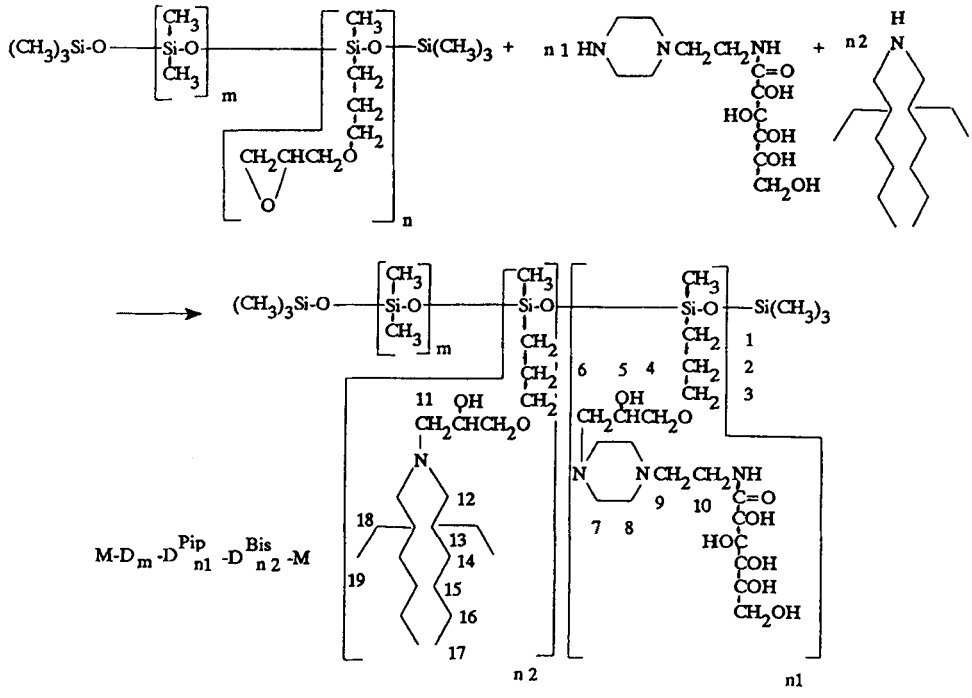
The reactions were carried out in a steel autoclave at 100 °C for 6 h. To avoid cross-linking in the final stage of the reaction, the gluconamide derivative was applied in a slight molar excess (ΣNH/Σepoxide= 1.05 : 1). The products were precipitated and washed in n-pentane, dried and characterized by means of ^{13}C NMR spectroscopy (e.g. Table 11).

This method was extended to mixed amine systems. The gluconamide derivative (**44**) was partially replaced by bis(2-ethylhexyl)amine, yielding polysiloxanes bearing hydrophilic carbohydrates as well as hydrophobic hydrocarbon subunits (Eqn [9]; Table 12).

Again the reactions were carried out in a steel autoclave at 100°C for 6 h. Prior to reaction, the amines were dissolved in the solvent (methanol). They were applied in a slight molar excess (ΣNH/

Table 11 ^{13}C NMR data (ppm) of a carbohydrate-modified polysiloxane (**71**)

C atom	1	2	3	4	5	6	7	8	9	10
	12.97	22.73	73.02	73.51	66.99	61.40	52.76	53.36	56.77	35.50



[9]

Table 12 Mixed modified polysiloxanes of the type $MD_mD^{Pip}_{n1}D^{Bis}_{n2}M$

Compound	*m*	*n1*	*n2*
75	0	7	3
76	0	6	4
77	0	5	5
78	0	4	6
79	0	3	7
80	20	10	10
81	20	8	12
82	11	5	2
83	11	4	3
84	11	3	4
85	11	2	5

Σepoxide= 1.1 : 1). The conversion of the bis(2-ethylhexyl)amine was followed by means of GC. In some cases, traces of remaining amine were found; in other experiments, no amine was detected at the end of the reaction. The solvent was removed and replaced by diethyl ether or n-pentane. Depending on the carbohydrate/hydrocarbon ratio, the products precipitated from or were dissolved in these solvents. The structure was determined by ^{13}C NMR data (e.g. Table 13).

RESULTS AND DISCUSSION

Siloxanyl-modified tertiary amines

As expected, the epoxides used alkylated the secondary amino function of the siloxanyl-modified carbohydrate derivative, under the conditions applied, quantitatively and regioselectively. With a single exception the reaction time did not depend on the epoxide structure. Only a bulky 1,1,1,3,5,5,5-heptamethyltrisiloxanyl structure (**8**) decreases the reaction rate, causing extended reaction time.

Table 13 ^{13}C NMR data (ppm) of a mixed substituted polysiloxane (**82**)

C atom	1	2	3	4	5	6	7	8	9	10
	12.96	22.73	73.05	73.40	66.97	61.40	52.76	53.36	56.78	35.49
C atom	11	12	13	14	15	16	17	18	19	
	60.06	52.76	36.81	28.49	30.83	22.59	13.75	24.05	10.61	

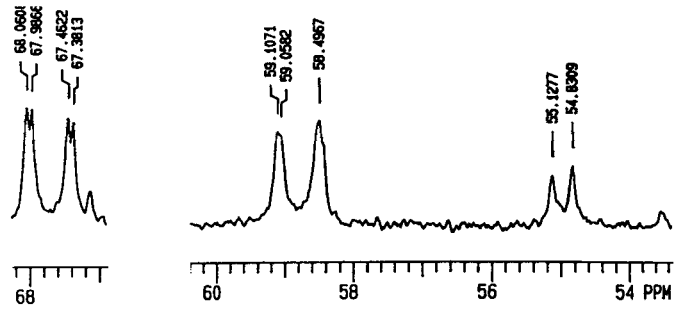


Figure 3 Enlarged regions of the ^{13}C NMR spectrum of compound **34**.

The ^{13}C NMR signal assignment was established by consideration of the data published in Part I of our series[6] and elsewhere.[11] In the spectra of the products (Table 2) we did not find significant signals for carbon atoms attached to new ether bridges (etherified hydroxyl groups) or secondary amino structures (starting material).[12] Many signals were multiplets (Fig. 3), due to the formation of diastereoisomers. The epoxides used possess an optically active carbon atom, and due to poor availability or extreme costs, pure *R* or *S* enantiomers were not used. As a result of the reactions three centres of optical activity are present in the molecules, i.e. (i) the carbon atom carrying the secondary hydroxyl group of the spacer, (ii) the carbon atom carrying the secondary hydroxyl group of the modifying element and (iii) the carbon atoms carrying the secondary hydroxyl groups of the carbohydrate unit (Eqn [1], compound **23**). No attempt has been made so far to separate the components of such a complex mixture of diastereoisomers.

In part I of our series[6] we have shown that the incorporation of a carefully chosen spacer between the siloxanyl and carbohydrate moieties can shift the hydrophilic–hydrophobic balance, as well as the organic solubility to a certain extent, in the desired direction. However, the presence of a secondary amino group opens up the possibility of introducing a powerful modifying element which supports or counterbalances the effects of the other three structural elements present.

The structure of the epoxide has a striking influence on the behaviour of the surfactant molecule towards different solvents (Table 14). As can be seen from this table, the introduction of an alkenyl (**15**) or aromatic (**17**) modifying element dramatically improves the solubility of the disaccharide derivative in weak polar organic solvents. A second trisiloxanyl unit (19) makes this disaccharide derivative insoluble even in water (but gives excellent solubility in C_5–C_{10} hydrocarbons). The character of the material changes from a hard solid (**13**) to a soft and sticky powder (**15–17**) and finally to a transparent wax (**19**). It is important to state that a glycidyl unit (**13**) is not hydrophilic enough to reduce substantially the organic solubility of a molecule already possessing this strong hydrophilic moiety (**9**).

Modified monosaccharide derivatives generally

Table 14 Solubility[a] of selected disaccharide derivatives in solvents of different polarity

Compound	H_2O	NMP	NOP	Hallcomid M8-10	Xylene	1,2,3-Trimethyl-benzene	isophorone	Octyl acetate	Rape-oil methyl ester	Paraffin oil
9	+	+	+	+	−	−	−	−	−	−
13	+	+	+	+	−	−	−	−	−	−
15	+	+	+	+	+	+	+	+	−	−
16	+	+	+	+	+	+	+	+	−	−
17	+	+	+	+	+	+	+	+	+	−
19	−	+	+	+	+	+	+	+	+	−

[a] Solubility of 7.15% surfactant in the solvent at room temperature. +, Soluble; −, insoluble. NMP, *N*-methylpyrrolidone; NOP, *N*-octylpyrrolidone; Hallcomid M8-10, C_8–C_{10} carboxylic acid amide.
Definitions here apply to Tables 14–19.

Table 15 Solubility of selected monosaccharide derivatives in solvents of different polarity

Compound	H_2O	NMP	NOP	Hallcomid M8-10	Xylene	1,2,3-Trimethyl-benzene	Isophorone	Octyl-acetate	Rape-oil methyl ester	Paraffin oil
20	+	+	+	+	+	+	+	+	–	–
23	+	+	+	+	+	+	+	+	+	–
24	+/–	+	+	+	+	+	+	+	–	–
25	+/–	+	+	+	+	+	+	+	+	–
26	–	+	+	+	+	+	+	+	+	–

+/– turbid dissolved.

show better solubility in organic solvents than analogous disaccharide species (Table 15). For aromatic substituents the solubility in water is already considerably reduced (**24** and **25**). A careful choice of the epoxide (**23**) is necessary. The character of the product changes from a soft and sticky powder (**20**) to sticky waxes (**24** and **25**) and finally to a viscous liquid (**26**).

As expected these trends, continue in the series of the γ-hydroxybutyric acid derivatives (Table 16). The spacer and a hydroxycarboxylic acid amide structure cannot counterbalance the hydrophobic siloxanyl unit combined with an aromatic modifying element. The solubility of such derivatives is further shifted to the non-polar side. With the exception of the glycidol derivative (**27**, wax), all derivatives synthesized are viscous liquids (i.e. syrups).

Compound **34** is a special case. In contrast to (**19**), the combination of two independent disiloxanyl units, one hydrophilic spacer and one powerful disaccharide moiety in (**34**) yields a water-soluble surfactant.

These few remarks have shown that by careful choice of the modifying element, the existing possibilities for the design of siloxanyl-modified carbohydrate surfactants can be extended considerably. As will be shown in a later paper, these modifications also have a striking influence on the interfacial properties.

However, from a strategic point of view one major disadvantage remains. The imbalance between the large group of powerful hydrophobic modifying elements and the smaller group of moderate hydrophilic ones persists.

Alkylation of hydrocarbon-based secondary amines

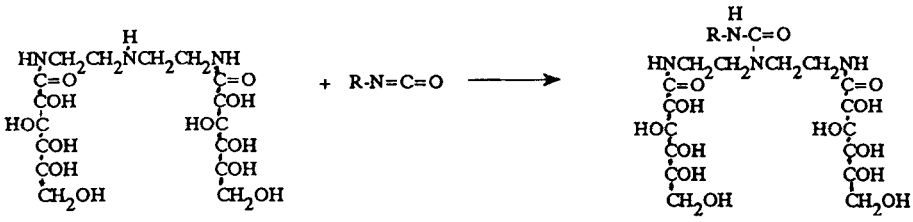
To overcome the above disadvantage we extended the scope of Ullsperger's method,[8] in which long chained hydrocarbon isocyanates or anhydrides reacted regioselectively with the secondary amino function of a monosaccharide-modified aminobisamide (Eqn [11]).

We first replaced D-gluconic acid δ-lactone by the weaker hydrophilic γ-butyrolactone and the stronger hydrophilic glucopyranosyl arabinonic acid lactone (Eqn [2]). Furthermore, diethylenetriamine can be replaced by dipropylenetriamine or triethylenetetramine (Eqn [4]). In these cases the aminobisamides formed tend not to precipitate spontaneously from methanol. Diethylenetriamine can also be replaced by 2-piperazin-1-ylethylamine or *N*-(2-aminoethyl)ethanolamine (Eqn [4]). Here only one hydrophilic unit is attached to the structure which will become part of the spacer and the modifying element.

γ-Hydroxybutyramides are slightly yellow, viscous liquids, while the other derivatives are white or slightly yellow powders.

Table 16 Solubility of selected γ-hydroxybutyric acid derivatives in solvents of different polarity

Compound	H_2O	NMP	NOP	Hallcomid M8-10	Xylene	1,2,3-Trimethyl-benzene	Isophorone	Octyl-acetate	Rape-oil methyl ester	Paraffin oil
27	+	+	+	+	+	+	+	+	–	–
28	+	+	+	+	+	+	+	+/–	–	–
29	+	+	+	+	+	+	+	+	–	–
30	–	+	+	+	+	+	+	+	+	–
31	–	+	+	+	+	+	+	+	+	+
32	–	+	+	+	+	+	+	+	+	+



[11]

In all cases we observed quantitative and regioselective conversions of the primary amino functions[8] (Table 5). The presence of secondary and/or tertiary amino functions did not have any significant influence on the course of the reactions.

In a second reaction step, these mono- and bisamides react with epoxysiloxanes yielding the corresponding tertiary amines (Eqns [5] and [6]).

In the cases of the bisamides (**62–64**) we were surprised by the straightforward reaction. Previously straight-chained carboxylic acid chlorides had given the appropriate products only in poor yields, and more reactive species, e.g. isocyanates, had to be used. Steric effects were thought to be the cause[8]. Consequently the considerably more branched siloxanyl-modified epoxides should also react slowly and with poor yields. Our results indicate that the nature of the electrophile is the more important factor (Eqn [10]).

On the other hand, attempts to add two moles of epoxide to the triethylenetetramine derivative (**55**) failed. ^{13}C NMR data show that the addition of one mole of epoxide yields the monoaddition product regioselectively. The addition of a second mole of epoxide proceeds only at elevated temperatures and in poor yields (according to ^{13}C NMR data there was less than 20% conversion; intensive signals for oxirane ring carbon atoms remain).

The incorporation of two carbohydrate units shifts the solubility to polar solvents (Table 17, compounds **62** and **63**).

The application of *N*-(2-aminoethyl)ethanolamine and 2-piperazin-1-ylethylamine yields products with an ethylene oxide or six-membered ring structure as the modifying element. The solubility data (compounds **59–61**) indicate that a single ethylene oxide unit attached to the surfactant molecule is less polar than a glycidol unit (**13**) or even the unmodified secondary amino function (**9**).

Piperazinyl derivatives (compounds **56–58**) show solubility profiles in organic solvents comparable with those of allyl glycidyl or phenyl glycidyl derivatives, but the solubility in water is slightly improved.

The major advantage of the strategies discussed in Parts I and II of our series is that a set of regioselective and almost quantitative reactions yields siloxanyl-modified carbohydrate surfactants consisting of four independent subunits: (i) a siloxane block [Si], (ii) a spacer [sp], (iii) a carbohydrate moiety [ch] and (iv) a modifying element [mo] (Fig. 4). Protecting/deprotecting steps are not necessary, lower alcohols are the favoured solvents, the reactions discussed in this section can be run as one-pot reactions without isolation of the aminoamides, and the starting materials are readily available.

Within the framework of this system the character of the surfactants can be shifted stepwise from hydrophilic to hydrophobic (Fig. 5). Compound **62** consists of one siloxanyl unit and two identical hydrophilic carbohydrate moieties (from a systema-

Table 17 Solubility of selected surfactants in solvents of different polarity

Compound	H_2O	NMP	NOP	Hallcomid M8-10	Xylene	1,2,3-Trimethyl-benzene	Isophorone	Octyl-acetate	Rape-oil methyl ester	Paraffin oil
62	+	+	–	–	–	–	–	–	–	–
63	+	+	–	–	–	–	–	–	–	–
59	+	+	+	+	+	+	+	–	–	–
60	+	+	–	–	+	+	–	+	–	–
61	+	+	+	+	+	+	+	–	–	–
56	+	+	+	+	+	+	+	+	–	–
57	+	+	+	+	+	+	+	+	+	
58	+/–	+	+	+	+	+	+	+	+	+

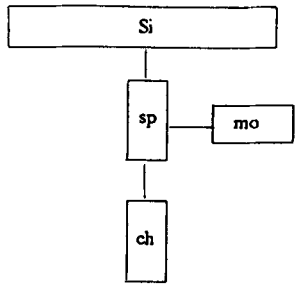


Figure 4 Schematic representation of the four independent subunits of the surfactants: Si, siloxane block; sp, spacer; ch, carbohydrate; mo,modifying element.

tic point of view, one carbohydrate unit is a modifying element). In compound **13** the second hydrophilic unit is weaker (shorter line) and produces a slight shift to the hydrophobic side. The incorporation of a methacrylic acid ester moiety (**14**, horizontal line) strengthens this trend. In compound **17** the aromatic unit (short upward line) represents a second hydrophobe. In compound **34** both hydrophobes are small disiloxanyl units. The surfactant remains water-soluble. Finally, in **19**, two identical hydrophobic trisiloxanyl units are attached to one carbohydrate moiety yielding a water-insoluble product. Considering the additional combinations of siloxanyl unit, spacer, carbohydrate and modifying element, further control of physicochemical properties is possible.

Alkylation of amine mixtures by polymeric epoxysiloxanes

In an attempt to apply some of the reactions discussed in the preceding section on polymeric structures, we tried to couple selected carbohydrate-modified aminomono- and aminobis-amides to polymeric epoxysiloxanes.

Unfortunately, explorative experiments showed that the branched aminobisamide structures yield considerable amounts of cross-linked products. The same is true for *N*-(2-aminoethyl)ethanolamine derivatives. In these cases, fractions of insoluble material as well as siloxanes containing partially unreacted epoxy functions were obtained.

The piperazinyl-modified glucoamide derivative **44** was found to be a nucleophile yielding the desired products without cross-linking (Tables 9 and 10). Obviously, steric effects start to play a major role because in sterically demanding situations cyclic secondary amines are known to be better nucleophiles than branched ones.[13, 14] It is reasonable that in the final stage of the reaction the secondary amino functions of less reactive nucleophiles and the already formed tertiary amino structures can act as catalysts for the uncontrolled cross-linking (oligomerization, reactions with OH groups) of epoxy groups.[15]

The ^{13}C NMR signal set of the polymeric product **71** (Table 11) is almost identical to that of compound **57**.

The comb-like structures synthesized were found to be soluble in water, whereas their organic solubility is limited (Table 18). This is mainly due to the relatively high carbohydrate content. To counterbalance this effect we tried to substitute carbohydrate units stepwise with alkyl groups. Secondary amines of different alkyl chain lengths and structures were tested. Diethylamine and even dibutylamine (Fig. 6, compound **86**) had little effect on the organic solubility whereas dicyclohexylamine yielded mainly insoluble products. Bis-(2-ethylhexyl)amine reacts without cross-linking and was found

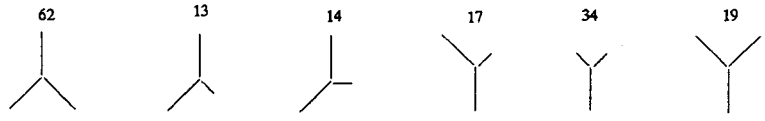


Figure 5 Shift from hydrophilec to hydrophobic character with structure; for explanation, see the text.

Table 18 Solubility of selected polymeric surfactants in solvents of different polarity

Compound	H_2O	NMP	NOP	Hallcomid M8-10	Xylene	1,2,3-Trimethyl-benzene	Isophorone	Octyl-acetate	Rape-oil methyl ester	Paraffin oil
69	+	+	–	–	–	–	–	–	–	–
71	+	+	–	–	–	–	–	–	–	–
72	+	+	–	–	–	–	–	–	–	–

Table 19 Solubility of selected polymeric surfactants in solvents of different polarity

Compound	H_2O	NMP	NOP	Hallcomid M8-10	Xylene	1,2,3-Trimethyl-benzene	Isophorone	Octyl-acetate	Rape-oil methyl ester	Paraffin oil
75	+	+	−	−	−	−	−	−	−	−
76	+	+	+	+	−	−	−	−	−	−
77	+	+	+	+	+/−	+/−	−	−	−	−
86	+	+	+	−	−	−	−	−	−	−
78	+	+	+	+	+	+	+	+	−	−
79	+/−	+	+	+	+	+	+	+	+/−	+/−
80	+	+	+	+	+	+	+	+	−	−
81	+/−	+	+	+	+	+	+	+	+/−	−
82	+	+	+	−	−	−	−	−	−	−
83	+	+	+	+	+	+	−	+	−	−
84	−	+	+	+	+	+	+	+	+/−	−
85	−	+	+	+	+	+	+	+	+	−

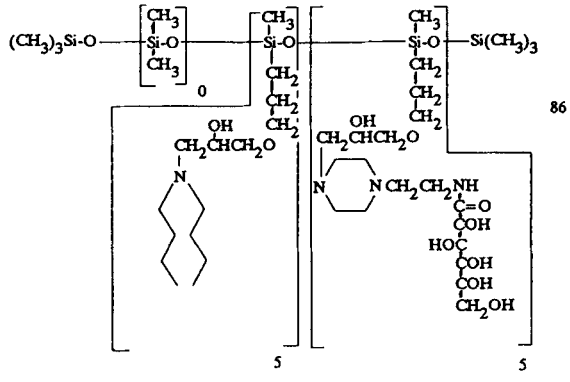


Figure 6 The structure of 86..

to be a powerful group for shifting the hydrophilic–hydrophobic balance (Table 19).

The ^{13}C NMR signal elucidation (Table 13) for these complex molecules was facilitated by the fact that the signal intensity showed a strong dependence on the hydrophilic amine/hydrophobic amine ratio.

According to the data shown in Tables 18 and 19, an increased proportion of alkyl units improves the organic solubility considerably. By careful choice of the ratio of *m*(dimethylsiloxanyl units)/*n*1(carbohydrate units)/*n*2(alkyl units), one can obtain almost every desired solubility profile. In line with solubility, the product character changes for a given polysiloxane from a hard powder (**75**) to a sticky wax (**79**).

It is necessary to point out that, with increasing relative proportions of dimethylsiloxanyl units, the possibilities of varying the ratio carbohydrate unit/alkyl unit with significant influence on the solubility profile are reduced. In certain cases minor changes make such substances insoluble in water whereas no substantial solubility gain is achieved on the non-polar side (substances **83–85**). Hydrophobicity caused by dimethylsiloxanyl units is different from that caused by hydrocarbon chains.[16]

To overcome this disadvantage we also tried to substitute the gluconamide derivative **44** with the more hydrophilic glucopyranosyl arabinonic acid species (**43**). To our surprise, repeated experiments ended with partially cross-linked and insoluble polymers. Obviously the more hindered disaccharide derivative is more closely related to the branched bisamide structures, **49–55**, and may act as a cross-linking catalyst. This finding emphasizes the basic rule that two amines of sufficient and probably comparable, nucleophilic strength have to be used.

Despite the above limitations, this concept opens up many new possibilities for the modification of polysiloxanes by hydrophilic as well as hydrophobic components.

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