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Simplified Synthesis of Amphiphilic Siloxanes with Methyl Gluconyl Glycinate Functionalities via Transacetalation

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ABSTRACT: New carbohydrate-functional siloxanes (CHFS) have successfully been synthesized by acid-catalyzed transacetalation between unprotected methyl gluconyl glycinate (MGG) as a hydrophilic component and an acetal-functional siloxane in DMF/dioxane mixed solvents. MGG, which can be regarded as a hybrid material composed of a saccharide and an amino acid, was easily synthesized in good yield by amide bond formation between D-glucono-1,5-lactone and glycine methylester hydrochloride. It was demonstrated that both amide and ester groups remained inactive under the transacetalation conditions. A rake-type CHFS as well as an ABA-type CHFS was obtained without an insolubilization problem indicating that the use of this modified carbohydrate is very advantageous in terms of the structural versatility. The materials thus obtained were soluble in both nonpolar solvents such as chloroform and polar solvents such as DMF and DMSO. The hydrophilicity of MGG, glucose, and poly(ethylene oxide) was estimated by the solubility parameter values and compared with the water solubility data. A simple emulsification study of CHFS suggested that these new materials are worth being investigated deeply to find applications, especially personal care and healthcare applications.

Introduction

Siloxane−polyether (SPE) copolymers are the most well-established siloxane surfactants to date.[1] These materials have been very useful in various applications such as textile treating agents, cosmetics, and polyurethane foam controlling agents, but there are some drawbacks, including the thermal instability during long-term storage above 50 °C and the poor emulsification activity at a siloxane/water interface. The former is due to the low thermal stability of the polyether component while the latter could be attributed to the weak intermolecular interactions between the surfactant molecules. Carbohydrate-functional siloxanes (CHFS) are one of the possible candidates to solve the above issues for the following reasons. First, carbohydrates, especially saccharide-based compounds, are stable below the melting temperatures, almost all of which are at around 150 °C. Second, very high intermolecular interactions via hydrogen bonding can be expected through many hydroxy groups of the carbohydrate molecules. In addition, there is a possible advantage of CHFS's environmental friendliness due to the biodegradability of both carbohydrate and siloxane moieties.

Despite these possible advantages for CHFS, limited number of publications concerning synthesis of CHFS have been made from both academic and industrial institutions.[2−12] We also reported a new synthetic method of CHFS by an acid-catalyzed transacetalation reaction using acetal-functional siloxanes and glucose.[13] This method has several advantages including the simplified process, high yield achieved, and inexpensive starting materials, but a notable issue of insolubilization was observed for the synthesis of rake-type and cyclic CHFS in which three or more glucose units were in the molecules. A reaction of acetal-functional siloxane derived from poly(oxydimethylsilylene-*co*-oxymethylhydrogensilylene) and glucose was summarized in Scheme 1.

A control experiment with a partially protected glucose indicated that the insolubilization problem observed in the synthesis with glucose is attributable to an unexpected reaction at the anomeric position (1-position) of glucose yielding a cross-linked material.[13] In other words, one cannot avoid the cross-linking of acetal-functional siloxane by glucose because the reactivity of the anomeric OH group seems comparable to that of the OH group at the 6-position under the present transacetalation conditions. Taking these results into account, a use of modified carbohydrates free from an anomeric OH group is thought to be an effective method to solve the problem. In this report is described synthesis of CHFS via transacetalation using methyl gluconyl glycinate (MGG) as a modified carbohydrate. A set of feasibility study on the emulsification activities of resulting new surfactants was also examined.

Experimental Section

Materials and Characterization. All liquid solvents for synthetic work are commercially available dehydrated reagents. Other chemicals are also commercially available reagent grade and used without further purification. Activated clay (K-500) was supplied from Nippon Kassei Hakudo Co. All Si−H functional siloxanes were supplied by Dow Corning and used after stripping at around 50 °C in vacuo.

Infrared (IR) spectra were obtained with a Jasco FT/IR-5300 spectrophotometer. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded with a Bruker ACP 300 spectrometer using tetramethylsilane as an external standard. The melting temperature of MGG was determined at a heating rate of 10 °C/min under nitrogen atmosphere by a Seiko DSC 6200. An elemental analysis was carried out by Sumika Chemical Analysis Service.

Synthesis of Acetal-Functional Siloxanes. Hydrosilylation between Si−H functional siloxanes and acrolein diethylacetal was performed as reported previously.[13] 1,1,1,3,5,5,5-Heptamethyltrisiloxane, Si−H terminated siloxane, and poly(oxydimethylsilylene-*co*-oxymethylhydrogensilylene) were used as siloxane components.

Synthesis of Ethyl Gluconyl Glycinate (EGG, Method A). D-Glucono-1,5-lactone (8.9 g; 50 mmol), glycine ethylester

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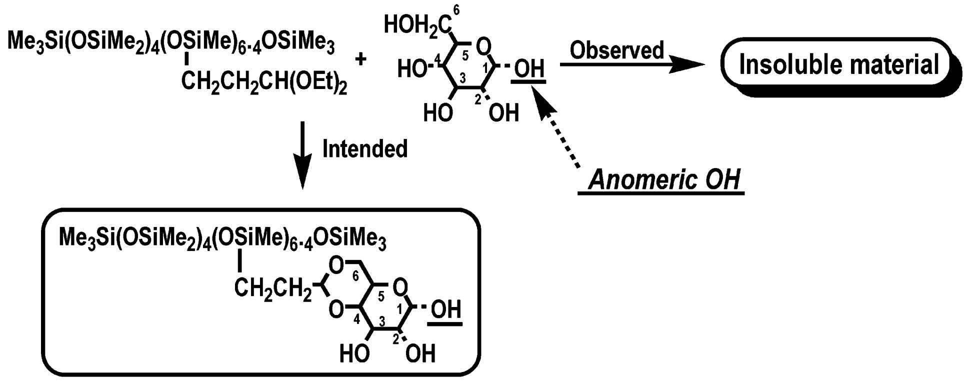
Scheme 1. Intended and Observed Reactions in the Synthesis of a Rake-Type CHFS Using Glucose



hydrochloride (7.0 g; 50.4 mmol), and triethylamine (8.3 mL; 60 mmol) were dissolved in a DMF (80 mL)/THF (40 mL) mixed solvent and heated at 80 °C under reflux for 2 h to yield a yellow solution. After cooling, a colorless needlelike solid, which is triethylamine hydrochloride, was filtered off, and almost all volatile components were removed in vacuo, yielding a thick orange solution. This was dissolved in an ethanol (40 mL)/chloroform (8 mL) mixed solvent at around 70 °C and stored in a refrigerator. A precipitate thus formed was separated by filtration and dried in vacuo at 80 °C to yield a colorless solid (7.05 g). A viscous orange liquid obtained from the supernatant underwent the similar recrystallization process using an ethanol (8 mL)/chloroform (8 mL) mixed solvent yielding a colorless solid (1.06 g). Total yield of EGG was 58%. ^{13}C NMR (DMSO-d_6; ppm): δ 14.2 (CH_2CH_3), 40.8 ($NHCH_2$), 60.8 (OCH_2), 63.6 (CH_2OH), 70.4, 71.7, 72.4, 73.6 (4 CHOH), 170.0 (CONH), 173.3 (CO_2).

Synthesis of Methyl Gluconyl Glycinate (MGG, Method B). Glycine methylester hydrochloride (25.0 g; 199 mmol) was dispersed in 150 mL of DMF and stirred at 80 °C for 10 min. The salt was partially soluble under these conditions. To the heterogeneous mixture was added triethylamine (28 mL; 201 mmol) to yield a colorless solid, and the resulting mixture was stirred at this temperature for a further 10 min. After cooling to room temperature, the solid was filtered off to afford a colorless solution. To the filtrate was added triethylamine (3 mL), and a solid formed was filtered again yielding a colorless solution. The total amount of solid, which proved to be triethylamine hydrochloride, was 24.99 g, which is 91% of a theoretical yield. Triethylamine (3 mL), THF (150 mL), and D-glucono-1,5-lactone (35.45 g; 199 mmol) were added to the colorless solution thus obtained, and the resulting homogeneous mixture was heated at 70 °C for 2 h.

All the volatile components were removed in vacuo yielding a yellow oily product. This product was dissolved in EtOH/$CHCl_3$ mixture (175/30 = v/v) at ca. 80 °C to yield a translucent solution. This was cooled to room temperature and then stored in a refrigerator over a weekend, yielding a yellow solution containing a colorless solid. The yellow supernatant was removed by filtration while the precipitate was washed with a EtOH/$CHCl_3$ mixed solvent (5/1 = v/v). The suspension thus obtained underwent centrifugation to separate the light yellow supernatant. This washing process was repeated once more to yield a colorless supernatant and a precipitate. The precipitate was finally dried in vacuo at 80 °C for 9 h, yielding a colorless solid (39.69 g).

The supernatants were combined and underwent evaporation to yield yellow viscous oil. The procedure for reprecipitation described above was employed to obtain MGG from the viscous material. A colorless solid (2.99 g) was obtained. Total yield of the solid product was 42.68 g (80% of theoretical amount). IR (KBr; cm^{-1}): 3507 (−OH), 3335−3200 (−NH), 2967, 2922, 1732 (−CO_2), 1636 (−CONH), 1545 (−NH & −CN), 1231 (−CO_2). ^{13}C NMR (DMSO-d_6; ppm): δ 40.9 ($NHCH_2$), 52.4 (OMe), 63.7 (CH_2OH), 70.6, 71.9, 72.6, 73.8 (4 CHOH), 170.9 (CONH), 173.8 (CO_2). Anal. Calcd for $C_9H_{17}NO_8$: C, 40.5; H, 6.4; N, 5.2. Found: C, 40.0; H, 6.5; N, 5.4. Melting temperature (onset temperature, °C): 186 dec.

Synthesis of CHFS (Trisiloxane-Based CHFS). MGG (16.17 g; 60.5 mmol) placed in a three-neck flask equipped with a Dean−Stark apparatus and a reflux condenser was dissolved in DMF (40 mL) at ca. 80 °C and the solution was diluted with ethanol (50 mL). The resulting hazy solution was heated at 110 °C for 55 min during which 39 mL of ethanol (and a trace amount of water contaminated) was distilled off. To the residual transparent solution were added 1,1,1,3,5,5,5-heptamethyl-3-(3,3-diethoxypropyl)trisiloxane (20.0 g; 55 mmol), dioxane (50 mL), and predried activated clay (7.0 g), and the resulting heterogeneous mixture was heated at 130 °C for 2.5 h during which 61 mL of ethanol/dioxane mixture was removed by distillation. A pale yellow clear solution containing activated clay was yielded.

A homogeneous solution obtained by filtration using a Kiriyama funnel underwent evaporation to remove solvents. The viscous product was diluted with toluene (ca. 40 mL), and an insoluble material was separated by centrifugation. This dilution/centrifugation process was repeated to minimize contamination of unreacted MGG. Removal of solvents yielded a dark yellow viscous liquid (27.95 g; 96%). IR (neat; cm^{-1}): 3401 (−OH), 2963, 2905, 1748 (−CO_2), 1661 (−CONH), 1539 (−NH and −CN), 1412, 1262, 1208 (−CO_2), 1092, 1024, 801. ^{13}C NMR (DMSO-d_6; ppm): δ −0.2 and 2.0 (SiCH_3), 11.1 and 11.6 (SiCH_2), 27.7 and 27.8 ($SiCH_2CH_2$), 40.9 ($NHCH_2$), 52.2 and 52.3 (OMe), 63.7 (CH_2O), 67−82 (CHOH carbons at 2, 3, 4, and 5 positions), 105.3 and 105.6 ($SiCH_2CH_2CH$), 170.5 and 170.7 and 170.9 (CONH), 173.5 and 173.7 (CO_2). ^{29}Si NMR (DMSO-d_6; ppm): δ 7.1 ($SiMe_3$), −21.0 ($SiMeCH_2CH_2CH$). Anal. Calcd for $C_{19}H_{41}NO_{10}Si_3$: C, 43.2; H, 7.8; N, 2.7. Found: C, 42.4; H, 7.5; N, 3.4.

Results and Discussion

(1) Synthesis of Alkyl Gluconyl Glycinate. As was described above, glucose proved an inappropriate component for the synthesis of CHFS via transacetalation because of the plural reactive sites yielding an insoluble material. Since native saccharides have similar structures leading to the identical problem essentially, one should look at other hydrophilic materials with single reactive site to solve this issue. In the present study, alkyl gluconyl glycinate, denoted as AGG hereafter, which can be regarded as a saccharide/amino acid combined material was examined due to its novelty as a component of surfactants and potentially high hydrophilicity. The structure of AGG is illustrated in Figure 1.

A possibly largest advantage of AGG is that the anomeric OH group is blocked as an amide bond. Since the primary reactive site of AGG should be an OH group at 6-position, one can expect that two types of transacetalation reactions take place at 4,6- and/or 5,6-positions without yielding an insoluble cross-linked material. Since this is based on an assumption that amide and ester groups are inactive under the transacetalation

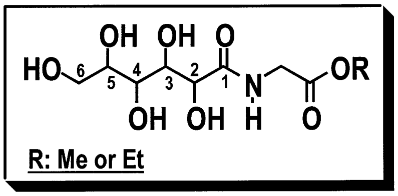


Figure 1. Structure of alkyl gluconyl glycinate.

Scheme 2. Synthesis of AGG by Method A

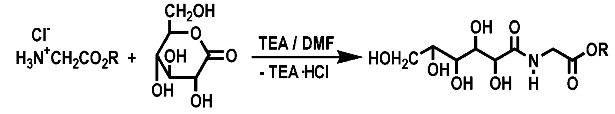
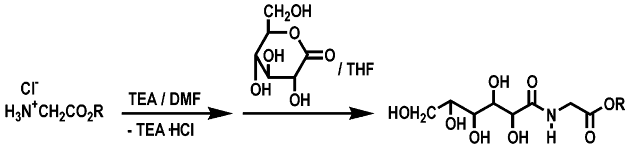


Table 1. Synthetic Results of a Ring-Opening Reaction Yielding AGG

run no.	alkyl (R)	method[a]	solvent	isolated yield (%)
1	Et	A	DMF	29
2	Et	A	DMF/THF	58
3	Me	B	DMF/THF	70
4	Me	B	DMF/THF	80

[a] A: All components were mixed and heated at 80 °C. B: A reaction was performed after removal of a TEA−HCl salt.

Scheme 3. Synthesis of AGG by Method B



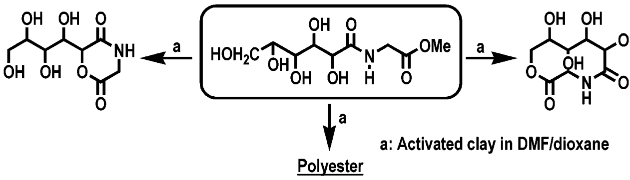
conditions, it is therefore necessary to ensure the stability before conducting the transacetalation.

A methyl derivative of AGG has been reported by Russian researchers in 1973.[14] They employed two methods for the synthesis, but both methods are three-step synthesis resulting in an overall yield of 40−60%. In the present study, an one-step synthesis was examined by a ring-opening reaction between D-glucono-1,5-lactone and glycine (m)ethylester hydrochloride in the presence of triethylamine (TEA) as an acid acceptor. First all reactants were dissolved in solvent(s) at an elevated temperature to yield AGG as shown in Scheme 2 (method A). The results are summarized in Table 1.

The spectral analyses of a solid product indicate that an intended reaction took place to yield desired ethyl gluconyl glycinate (EGG), but an isolated yield was very low in run 1 due to the difficulty of separation of EGG from triethylamine hydrochloride (TEA−HCl). A use of a THF/DMF mixed solvent in run 2 increased the solubility difference between EGG and TEA−HCl resulting in improved removal of TEA−HCl from the reaction solution and therefore increased isolated yield of EGG. Since the yield in run 2 was still an unsatisfactory level, the synthetic procedure was modified as is shown in Scheme 3 (method B) where glycine methylester hydrochloride was used.

Approximately 91% of TEA−HCl was separated from a DMF solution of glycine methylester hydrochloride before reacting with D-glucono-1,5-lactone. The isolated yield of methyl gluconyl glycinate (MGG) in run 3 was higher than that in run 2 as was expected. The yield was further increased to 80% in run 4 by changing the solvent from ethanol to an EtOH/$CHCl_3$ mixture (175/30 = v/v) in the recrystallization process.

Scheme 4. Possible Undesirable Reactions of MGG under an Acidic Condition



Both EGG and MGG were soluble in DMF, DMSO, and water indicating that they have high hydrophilicity despite their ester form. Taking the possibly higher hydrophilicity of MGG than EGG into account, this was chosen as a new hydrophilic component of CHFS.

(2) Stability of MGG under the Transacetalation Conditions. The advantage of AGG described above will be reduced if either amide or ester bond reacts during transacetalation. To demonstrate the stability of amide and ester groups under acidic transacetalation conditions, MGG was heated in a DMF/dioxane mixed solvent in the presence of activated clay, a suitable transacetalation catalyst. Possible undesirable reactions are illustrated in Scheme 4.

No insoluble product formed by this reaction. It is very encouraging that the solid product was an unreacted MGG although some new resonances with very small intensities were observed in the ^{13}C NMR spectrum. This result suggests that amide and ester groups of MGG are substantially inactive under transacetalation conditions. One can expect synthesizing MGG-based CHFS free from undesired cross-linking.

(3) Synthesis of MGG-Based CHFS via Transacetalation. Transacetalation between an acetal-functional siloxane and MGG was examined first using 1,1,1,3,5,5,5-heptamethyl-3-(3,3-diethoxypropyl)trisiloxane as a siloxane component. A DMF/dioxane mixed solvent was used to solubilize both components while activated clay was used as an acid catalyst. The intended reaction is shown in Scheme 5.

The reaction proceeded without phase separation as was observed in the reaction using glucose. The ^{13}C NMR spectrum of the product is depicted in Figure 2.

No sign of resonance assignable to a methyl carbon of ethoxy groups and observation of new resonances assignable to acetal carbons suggest that the siloxane was connected to MGG by cyclic acetal formation. It is notable that resonances assignable to a methyl carbon of methyl ester and carbonyl carbons of amide and ester moieties were observed at chemical shifts each of which was exactly identical to those of original MGG. This also indicates that both amide and ester moieties of MGG remained unchanged by the transacetalation as was expected. The split resonances for ethylene, acetal, amide, and ester moieties are probably indicative of the formation of two species described in Scheme 5. Elemental analysis data of the product are also consistent with the structures in the scheme. The most intriguing and advantageous observation is that no resonance assignable to an aldehyde group was detected in the spectrum. The aldehyde formation is one of disadvantages observed in this transacetalation route using glucose. The reason the formation was avoided has not been identified, but exhaustive removal of moisture from MGG may be easier than that from glucose.

The transacetalation was also examined with other diethylacetal-functional siloxanes. Diethylacetal-termi-

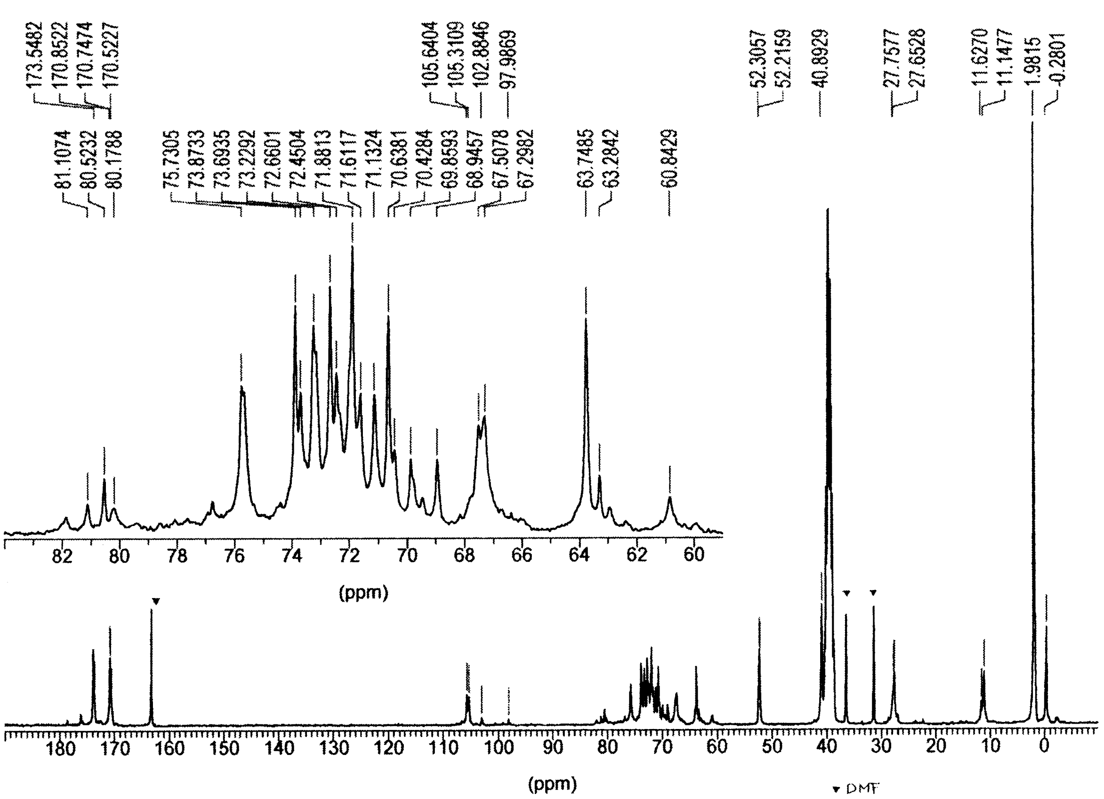
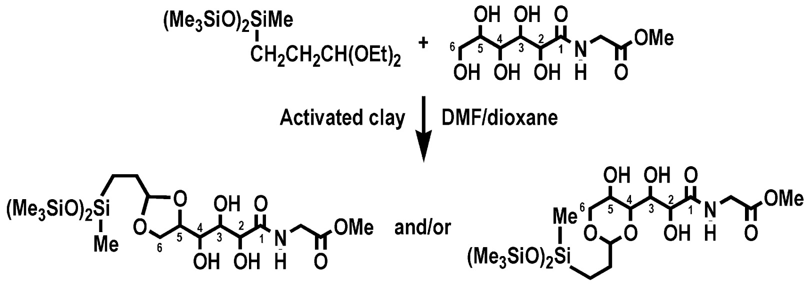


Figure 2. ^{13}C NMR spectrum of MGG-functional trisiloxane.

Scheme 5. Possible Reaction Products for Transacetalation of MGG



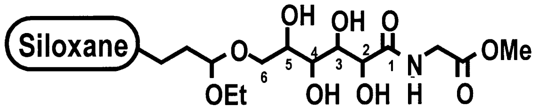


Figure 3. Possible structure of monoethyl acetal species.

nated siloxane was reacted with MGG to obtain an ABA-type material where A is a carbohydrate component and B is a siloxane component. On the other hand, a rake-type structure was yielded by using poly(oxydimethylsilylene-*co*-oxymethyl[3,3-diethoxypropyl]silylene) as a starting material. Synthesis of the two types of materials was accomplished without insolubilization problem as was expected. This should be attributed to the suppression of a reaction at an anomeric position by using MGG. In the rake-type case, a small amount of ethoxy group remained in the product as was suggested by the ^{13}C NMR analysis. This should be due to the steric hindrance of diethylacetal groups on the siloxane main chain yielding monoethyl acetal linkages as shown in Figure 3. One cannot completely exclude the presence of residual diethylacetal groups in the product, but the probability is statistically very low.

(4) Properties of MGG-Based CHFS. Solubilities. The solubilities of three MGG-based CHFS in various solvents at room temperature are listed in Table 2 along with those of two glucose-based CHFS.

Table 2. Solubilities of Various CHFS at Room Temperature[a]

CHFS no.	1	2	3	4[d]	5[d]
structure[b] X	MD^XM MGG	$M^XD_{15}M^X$ MGG	$MD_9D^X_4M$ MGG	MD^XM glucose	$M^XD_{15}M^X$ glucose
CH content[c]	53	30	49	43	23
toluene	◇	◇	◇	◇	◇
chloroform	◇	◇	◇	◇	◇
THF	◇	◇	◇	◇	◇
dioxane	◇	◇	◇	◇	◇
DMF	◇	◇	◇	◇	◇
DMSO	◇	◇	◇	◇	○
DMSO-d_6	◇	○	◇	◇	○
water	●	●	●	●	●

[a] Examined with the solute content of ca. 5−10 wt %. Key: (◇) soluble; (○) partially soluble; (●) insoluble. [b] A carbohydrate component denoted as "X" is connected at a γ-carbon on M or D units of siloxanes. M^X represents $XCHCH_2CH_2Me_2SiO_{1/2}$ while D^X represents $XCHCH_2CH_2MeSiO$. [c] Carbohydrate content (wt %) of major species. [d] These two CHFS were synthesized according to the method described in ref 13.

All MGG-based CHFS were soluble in DMF and DMSO, indicating that hydrophilicity was imparted to

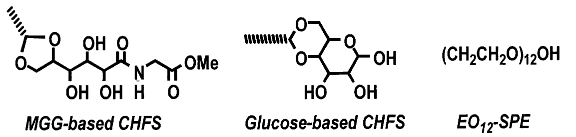


Figure 4. Structures of hydrophilic components of CHFS and SPE.

siloxanes by the introduction of MGG. Since the CHFS were also soluble in hydrophobic solvents, they are regarded as amphiphilic materials. The observed poor solubility in water will be due to an insufficient concentration of the hydrophilic moiety and the configurationally small MGG unit. It is of interest to note that DMSO is a good solvent for CHFS 2, but DMSO-d_6 is not.[15] It is also notable that CHFS 2 was soluble in DMSO while CHFS 5, a glucose analogue of 2, was partially soluble in the solvent. This solubility difference can be explained by the structures of the molecules. CHFS 2 will be a genuine ABA-type material, whereas a part of the anomeric OH groups of CHFS 5 reacted to yield oligomeric species such as an ABABA-type material as descried previously.[13] Because of the contamination of these species, the actual CH content of CHFS 5 would be lower than the estimated value of 23 wt %. This suggests that MGG is much more advantageous than glucose as the hydrophilic component of CHFS.

Quantification of the Hydrophilicity. It is well-known that the solubilities of solutes in organic liquids directly relate to the cohesive properties. The cohesive properties are expressed quantitatively in the cohesive energy ($\mathbf{E}_{coh}$) and the cohesive energy per unit volume is called cohesive energy density. Hildebrand gave a comprehensive treatment of the concept of cohesive energy density and proposed the square root of this as a “solubility parameter (δ)”.[16] The concept of the solubility parameters is now extended to polymeric materials to understand and estimate the solubilities of polymers.[17]

The solubilities of polymers strongly depend on their chemical structures. In general, structural similarity favors solubility. In other words, the solubility of a given polymer in a given solvent is favored if the solubility parameters of polymers and solvent are close. Since δ is positively related to $\mathbf{E}_{coh}$, materials with functional groups as hydrogen-bonding sites generally have high δ values. One can therefore assume that materials with high δ values are in general more hydrophilic than those with low δ values. Taking these facts into accounts, the δ values of hydrophilic components in CHFS were calculated in order to quantify the hydrophilicity of MGG, glucose, and polyether.

The structures of the hydrophilic components are summarized in Figure 4.

An ethylene unit for CHFS and a trimethylene unit for SPE are not depicted in the figure because they were regarded as hydrophobic components. There is another structural unit in the MGG-based CHFS as described in Scheme 5, but the change in the size of ring structure does not affect the δ value.[18] In addition, since the δ value does not depend on the number of repeating units for polymers, a typical example of EO_{12} with an OH terminal is represented as a hydrophilic component of SPE.[19]

Table 3. Numbers of Groups in Each Hydrophilic Component

group	MGG-based CHFS	glucose-based CHFS	EO_{12}-based SPE
$-CH_3$	1		
$-CH_2-$	2	1	24
-CH=	5	6	
$-OH$			1
$-OH$[a]	3	3	
$-O-$	2	3	12
$-CONH-$	1		
$-COO-$	1		
ring closure	1	2	

[a] OH groups on one C atom or on adjacent C atoms.

Table 4. Solubility Parameters of Three Hydrophilic Components Calculated by Two Methods

	MGG-based		glucose-based		EO_{12}-based	
	Fedors	H. & V.K.[a]	Fedors	H. & V.K.[a]	Fedors	H. & V.K.[a]
δ[b]	31.6	28.6	33.4	24.8	20.7	19.6

[a] Hoftyzer and Van Krevelen. [b] Values in $J^{1/2}/cm^{3/2}$.

Prediction of the $\mathbf{E}_{coh}$ and the molar volumes ($\mathbf{V}$) by means of additive functions has been developed by several groups.[17] In the present study, group contributions to these two parameters by Fedors[18] and Hoftyzer and Van Krevelen[17] were used because these two research groups extensively examined the group contribution methodology. The parameters of various structural groups were referred from references[17,18] while the numbers of these groups ($\mathbf{n}$) in each hydrophilic component are listed in Table 3. The $\mathbf{E}_{coh}$ and $\mathbf{V}$ of each component can be calculated by using the following equations.

$$\mathbf{E}_{coh}(\text{component}) = \Sigma[\mathbf{E}_{coh}(\text{group}) \times \mathbf{n}] \qquad (1)$$

$$\mathbf{V}(\text{component}) = \Sigma[\mathbf{V}(\text{group}) \times \mathbf{n}] \qquad (2)$$

The δ values derived from the equation below are summarized in Table 4.

$$\delta = [\mathbf{E}_{coh}(\text{component})/\mathbf{V}(\text{component})]^{1/2} \qquad (3)$$

The δ values of the hydrophilic components of MGG-based CHFS and EO_{12}-based SPE were not affected by the calculation methods used while a significant difference was observed between the values of glucose-based CHFS. The deviations of δ values derived from the calculation methods are due to differences in both $\mathbf{E}_{coh}$ and $\mathbf{V}$ values of several groups, especially of methyn group (−CH=). Despite these deviations, it can be concluded that the δ values of both hydrophilic components of CHFS are tangibly larger than those of SPE suggesting that the hydrophilicity of carbohydrate-(**CH**-) based components will be larger than that of poly(oxyethylene) (POE) unit.

Taking these quantification data, one can discuss again the actual solubility of CHFS and SPE. As described in the previous section, all CHFS were not soluble in water although the **CH** contents of trisiloxane-type and rake-type materials are as high as 43−53 wt %. On the other hand, a SPE with the POE content of around 34 wt % can be solubilized in water. A hypothesis can be made that water solubility is dominated by the (1) content and (2) volume of the hydrophilic components and (3) the degree of intermolecular interactions. These **CH** moieties are much smaller in size than POE indicating that the relative size of the hydrophilic component to the hydrophobic component for the former is smaller than that for the latter. In addition, the **CH** moieties would have larger intermolecular interactions than POE because of the presence of plural OH groups. Hence, as for water solubility, CHFS seems better than SPE in terms of the content of hydrophilic component, but inferior in terms of volume of the hydrophilic components and interactions with water molecules. These would explain the observed poor solubility of CHFS in water.

Emulsification Activities. A simple test was made by preparing mechanical emulsions comprising water, poly(dimethylsiloxane) oil, and the CHFS to gain insights into the emulsification activities of the CHFS. Three MGG-based materials described in Table 2 were examined with corresponding SPEs for both W/O (water in oil) and O/W (oil in water) formulations. The results are summarized in Table 5.

Table 5. Behavior of Mechanical Emulsions at Room Temperature[a]

materials	W/O[b]	O/W[b]
CHFS: trisiloxane	PS[c] within 1 day	PS[c] immediately
CHFS: ABA-type siloxane	PS[c] within 1 day	gelation
CHFS: rake-type siloxane	PS[c] after 2 days	PS[c] immediately
SPE: trisiloxane	PS[c] after 2 days	PS[c] immediately
SPE: ABA-type siloxane	PS[c] after 5 days	PS[c] immediately
SPE: rake-type siloxane	PS[c] within 1 day	PS[c] immediately

[a] Each emulsion (5 g each) was prepared by a vibration shaker and allowed to settle at room temperature. [b] W/O formulations: poly(dimethylsiloxane) (100 cSt)/water/CHFS or SPE = 73/23/4 (in weight); O/W formulations: poly(dimethylsiloxane) (100 cSt)/water/CHFS or SPE = 23/73/4 (in weight). [c] PS = phase separation.

In W/O formulations, an emulsion containing the rake-type CHFS was stable for more than 2 days while emulsions containing trisiloxane and ABA-type CHFS became phase separated mixtures within 1 day. The stability of the emulsion containing the rake-type CHFS was nearly comparable to that containing the trisiloxane SPE. In O/W formulations, all emulsions based on SPEs and two of three emulsions based on CHFS became phase separated mixtures soon after preparation. On the other hand, it is of great interest that an emulsion containing the ABA-type CHFS turned into a gel containing a small amount of water and the gel was stable for more than 2 months. These simple tests suggest that the ABA-type CHFS is worth being studied deeply to find personal care and healthcare applications such as a wound cure application although the present three CHFS do not seem to be very good emulsifiers.

Conclusions

CHFS with a new hydrophilic moiety was synthesized by transacetalation between an acetal-functional siloxane and hydrophilic methyl gluconyl glycinate (MGG). An advantage of MGG is one dominant reactive site at primary OH group resulting in the formation of only soluble products without protection of many other OH groups of MGG. In addition this is soluble in water despite its ester form indicating that this is highly hydrophilic. The calculation of solubility parameters for MGG, glucose, and poly(oxyethylene) (POE) supports an assumption that the hydrophilicity of MGG is much larger than that of POE. The solubility and emulsification activities were examined by using three CHFS along with three SPE materials. Although these CHFS are not likely to be good emulsifiers, an interesting phenomenon of gel formation was observed when an ABA-type CHFS was used. These new materials are worth investigating in detail focusing on the structure–property relationship because CHFS have two attractive components: very hydrophobic siloxane with the surface tension as low as 21 dyn/cm and highly hydrophilic methyl gluconyl glycinate containing many OH plus an amide groups.

References and Notes

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