Characterization of Novel Cationic Aminohydroxysiloxanes

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ABSTRACT: A new family of nonionic and cationic amino–hydroxy functional siloxanes have been prepared and characterized. The surface-active properties of such siloxanes can be tailored, enabling their use as a new generation of surfactants. Three siloxane polymers having the empirical formula of $Me_3SiO(SiMe_2O)_x(SiMeHO)_ySiMe_3$, where (1) $x = 0, y = 0$, i.e., $Me_2HSiOSiHMe_2$; (2) $x = 0, y = 33$; and (3) $x = 150$, $y = 23$, were hydrosilylated with allyl glycidyl ether to form epoxysiloxanes in high yields. Various amines react with these epoxysiloxanes to give nonionic aminohydroxysiloxanes also in good yield. Cationic species are obtained upon protonation of the amino nitrogen on the nonionic siloxane side chain, with hydrogen bromide solution. Characterization of all surfactants by FT-IR and NMR spectroscopy is reported. In addition, two-dimensional NMR studies could accurately elucidate the structure of the organic side groups present.

Introduction

Siloxanes have been widely used for many years as surfactants because of their high surface energy and activity as well as their stability toward heat, chemicals, and UV radiation. The specific surface free energy of siloxanes (surface tension of ~21 mN/m)[1] is significantly lower than that of most hydrocarbons, which means not only that they will be positively adsorbed at hydrocarbon surfaces but also that siloxanes lower the surface tension of their solutions. This property makes siloxanes very useful as surfactants.

Siloxane surfactant properties stem from the electronic and structural properties of the Si–O and Si–C bonds, which impart to the surfactant its specific physical, chemical, and mechanical properties. The Si–O bonds act to reduce steric conflicts between methyl groups on neighboring silicon atoms, by permitting unhindered rotation about the Si–O and Si–C bonds. Furthermore, the partial ionic character of the Si–O bond itself allows distortion of the large bond angle at oxygen to further relieve any additional steric hindrance. This freedom of rotation about the Si–O and Si–C bonds gives ideal screening of the polar Si–O–Si backbone by the nonpolar methyl groups, giving siloxane polymers excellent film-forming properties. These unique surfactant properties have been investigated with ionically charged hydrophilic groups including cationic and anionic species.[2] Our interest resides with cationic amino–hydroxy functional siloxanes, which have a variety of applications associated with the reactivity of the hydrophilic amino groups coupled to the inert hydrophobic siloxane backbone.

In the past the synthesis of amino functional siloxanes was accomplished by a variety of methods. Typically, aminosiloxanes have been prepared by reacting hydroxy functional siloxanes with aminosilane coupling agents.[3] Unfortunately, this process suffers from steadily increasing molecular weight and polydipersity in the polymer resulting in viscosity drift of the product. Similar viscosity drift occurs with aminosiloxanes prepared by reducing nitrile groups on siloxane side chains with $LiAlH_4$.[4] Such molecular redistribution reactions are quite common with siloxane reactants. Aminosiloxanes have also been prepared by hydrolysis of (aminomethyl)silanes[5] as well as by hydrosilylation.[6] Our earlier hydrosilylation route involves the reaction of a hydridosiloxane with an unsaturated ketinimine ($R_2C{=}NCH{=}CH_2$) in the presence of a platinum catalyst. The resultant ketinimine siloxane is then converted into an aminosiloxane by hydrolysis. The hydrolysis step, however, is very dependent on the molecular weight of the siloxane, as increasing molecular weight decreases the affinity of the starting siloxane toward hydrolysis, reducing the final yield and purity of the product. McGrath and Spinu[7] have also recently synthesized long-chain siloxanes with pendant amine groups but using a coequilibration anionic polymerization reaction in the presence of a silanolate catalyst.

A convenient step to synthesizing aminosilane compounds was described by Pleuddemann in 1960.[8] Pleuddemann reacted a range of epoxysilanes with various amines to give the corresponding aminohydroxysilanes through epoxy ring opening. Ring-opening reactions of epoxysilanes with dimethylamine, methanol, and $LiAlH_4$ have been carried out to give amino- and hydroxysilanes in high yields (>80%).[9] Subsequently, the ring-opening reaction of epoxysiloxanes with certain amines has been extended to produce cyano functional side groups.[10] To our surprise the perceptive extension of this epoxysilane chemistry to its siloxane counterparts has been virtually ignored in the extant literature. Riffle and co-workers[11] have, however, prepared telechelic aminosiloxane oligomers by this route. They indicate that complete NMR and FT-IR characterization of the prepared piperazine siloxane derivatives was obtained. The absence of actual spectroscopic detail, however, makes monitoring such reaction chemistry difficult, especially where end-group analysis by NMR is used to determine the formation of high molecular weight siloxanes. For this reason, we have set out to synthesize pendant aminosiloxane polymers, where the versatility of modern spectroscopic techniques such as 2D NMR can be used to monitor the formation of the amine pendant groups and also to clearly define the final prepared polymers.

Two-dimensional Fourier transform NMR offers great advantages for the analysis of organosilicon compounds, because of the increased resolution and the ability it has to correlate different nuclei directly.[17] To date, 2D NMR has been used very sparingly for the analysis of organosiloxanes, particularly for the analysis of pendant organic groups on a siloxane backbone. The majority of the published applications of 2D NMR have been concerned

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with the analysis of silicon derivatization of oligosaccharides.[18,19] However, we feel that 2D NMR offers a quick and relatively simple method of characterizing organosilicon polymers very effectively, and we have used this technique to analyze the pendant amine groups on a variety of siloxane macromers. Structural assignment of the pendant amino groups is made possible by a synergetic combination of 2D NMR correlated experiments, COSY (^1H–^1H) and HETCOR (^1H–^{13}C).

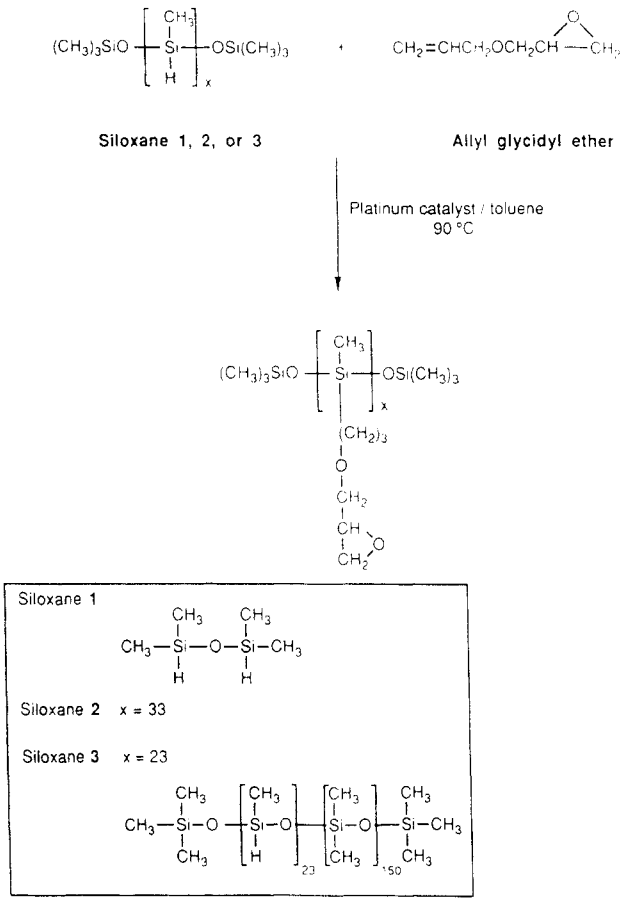
Ammonium siloxane polymers find widespread use in hair care formulations.[2] Often such cationic aminosiloxanes are prepared by the simple addition of a haloacid, such as hydrogen bromide, to an amine-terminated siloxane, converting the amino group to its ammonium bromide salt.[12–14] Similarly zwitterionic organofunctional siloxanes have also been prepared by the quaternization of amine functional siloxanes with 1,3-propene sulfone[15] and 1,4-butane sulfone.[16] In this paper we report the first preparation and characterization of a wide range of now readily-accessible aminohydroxysiloxanes using the amine–epoxy ring-opening reaction. Subsequently, the simple addition of HBr generated the cationic siloxane surfactants.

Experimental Section

Instrumentation. Fourier transform infrared spectroscopy was carried out with the use of a BIORAD Model FTS65 FT-IR spectrometer using NaCl plates. Spectra were obtained over the wavenumber range from 700 to 4000 cm^{-1} (resolution of 2 cm^{-1}) with the use of a MCT liquid-nitrogen-cooled detector with a coaddition of 64 scans. Nuclear magnetic resonance analyses was conducted with a Varian Gemini Fourier transform NMR spectrometer (200 MHz) and associated software. All spectra were obtained with the use of $CDCl_3$ (Cambridge Isotope Laboratories) as solvent and internal standard (^1H NMR δ 7.26; ^{13}C NMR δ 77.00) unless stated otherwise. The number of transients for ^1H and ^{13}C NMR spectra were generally 16 and 2000, respectively. All 2D NMR experiments were performed using standard software provided by the manufacturer (Version 6.2). Homonuclear ^1H–^1H correlated spectra were measured using the COSY pulse sequence. The spectral width was varied between 750 and 1000 Hz. Generally, the number of transients (NT) and number of increments (NI) were 160 and 300, respectively. The heteronuclear ^{13}C–^1H chemical shift correlated spectra were measured with the HETCOR pulse sequence. The spectral width in the ^{13}C dimension varied between 10 000 and 15 000 Hz with NT = 256 and NI = 64. The decoupler frequency and spectral width in the 2D spectrum were set to match those used in the measurements of the corresponding 1D spectrum. Elemental analyses were obtained from the microanalytical service of the Department of Chemistry at the University of Queensland. Gel permeation chromatography was carried out with the use of a Waters Model 6000A chromatograph with an R401 differential refractometer detector. The column set comprised 10^3- and 10^4-Å Ultrastyragel columns (Waters Associates). Sample concentrations were approximately 3% by weight in toluene, and the typical injection volume for the siloxane was 5 μL. The mobile-phase toluene was purified by distilling and filtering through a sintered-glass crucible. Standardization of the GPC was accomplished by use of styrene standards of known molecular weight (Waters Associates). The standards were made to a 10% w/w solution in toluene, and 5 μL was injected into the GPC.

Reagents. All reagents were of at least laboratory grade. The following reagents were used as supplied: hexachloroplatinic acid, platinum on carbon, allyl glycidyl ether, tetramethyldisiloxane (Aldrich); hexylamine, phenol (Fluka Buchs); dicyclohexylamine (Unilab); benzylamine (Kochlight); methylamine (25% solution; May and Baker); octamethylcyclotetrasiloxane (Toshiba); poly(methylhydrogensiloxane) (GE1040, degree of polymerization dp = 33) and hexamethyldisiloxane (General Electric); hydrogen bromide (48% solution), Celite, bentonite clay, and sodium hydroxide (ACE Chemicals). Dry toluene was obtained by distillation (bp 110 °C) and storing over 4-Å molecular sieves.

Scheme 1. General Preparation Scheme for Epoxysiloxanes



Triethylamine (Aldrich) was distilled (bp 89 °C) and dried over 4-Å molecular sieves. Tetrahydrofuran was dried by distilling (bp 67 °C) over sodium wire with benzophenone until a violet color develops indicating the formation of a ketyl radical.[20]

Overall Synthesis Procedure. A three-step procedure was employed. The first step involves hydrosilylation of Si–H functional siloxanes with allyl glycidyl ether in the presence of a platinum catalyst. The second step involves the attachment of various amines (primary, secondary, and tertiary) to the epoxysiloxanes. In the final step, cationic aminosiloxanes are formed by the addition of a hydrogen bromide solution to the nonionic aminosiloxanes prepared in the second step.

Preparation of Si–H Functional Siloxanes. A mixture of poly(methylhydrogensiloxane) (dp = 33, 68 g, 0.0314 mol), octamethylcyclotetrasiloxane (500 g, 1.69 mol), hexamethyldisiloxane (2.24 g, 0.014 mol), and bentonite clay (18 g, 1.5% w/w bentonite clay/reagents) was stirred at reflux (100 °C) for 16 h. After cooling to room temperature the mixture was filtered through a 10-mm polypropylene filter bag. The colorless clear oil (89.0%) was then dried in vacuo to remove any excess octamethylcyclotetramethylsiloxane. Characterization of the product was carried out by NMR, FT-IR, and GPC: ^1H NMR δ 0.1 (s, $SiCH_3$), 4.7 (s, SiH); ^{13}C NMR δ 0.1 ($SiCH_3$); FT-IR (cm^{-1}) ν 2990 (m), 2160 (s), 1460 (m), 1260 (s), 1100 (s). Analysis by GPC of the product consisted of one low molecular weight fraction (M_w): 1.23×10^4.

Epoxysiloxanes (1–3). A solution containing one of either tetramethyldisiloxane (5.0 g, 37.00 mmol), poly(methylhydrogensiloxane) (4.8 g, 2.24 mmol; dp = 33), or poly(methylhydrogensiloxane-*co*-dimethylsiloxane) (2.5 g, 0.197 mmol) made up with platinum on carbon (10 mg) in toluene (5 mL) was stirred under nitrogen at 90 °C in a two-necked, 50-mL flask (Scheme 1). Allyl glycidyl ether in a 2 M excess was added slowly and the mixture stirred under nitrogen for 16 h. The reaction was adjudged complete by monitoring the disappearance of the Si–H resonance in the ^1H NMR spectrum. The platinum catalyst was removed via vacuum filtration (sintered-glass filter packed with a Celite bed), by washing with toluene. The toluene was then

removed in vacuo. Polymers 1–3 were isolated after the solvent was removed in vacuo at 90 °C and were clear oils. NMR and FT-IR were used to characterize the products.

Siloxane 1: clear colorless oil, 70.4%; ^{1}H NMR δ 0.1 (s, $SiCH_3$), 0.5 (br, CH_2CH_2Si), 1.6 (br, CH_2CH_2Si), 2.7 (d, epoxy-CH_2), 3.1 (br, epoxy-CH), 3.4 (br, $Si(CH_2)_2CH_2OCH_2$); ^{13}C NMR δ −0.4 ($SiCH_3$), 13.4 (CH_2CH_2Si), 23.2 (CH_2CH_2Si), 44.2 (epoxy-CH_2), 51.5 (epoxy-CH), 72, 74 ($Si(CH_2)_2CH_2OCH_2$); FT-IR (cm^{-1}) ν 2990 (m), 1410 (m), 1260 (s), 1150 (m), 1100 (s), 910 (m); GPC M_w = 363 (theoretical M_w = 362).

Siloxane 2: clear colorless oil, 67.7%; ^{1}H NMR, ^{13}C NMR, and FT-IR are identical to those of siloxane 1; GPC M_2 = 5550 (theoretical M_w = 5904).

Siloxane 3: clear colorless oil, 88.0%; ^{1}H NMR, ^{13}C NMR, and FT-IR are identical to those of siloxane 1; GPC M_w = 1.58 × 10^4 (theoretical M_w = 15 264).

Preparation of Nonionic (Hexylamino)hydroxysiloxanes (4, 8, and 12). Into a two-necked flask was added one of the following siloxanes: 1 (1.52 g, 4.10 mmol), 2 (0.2 g, 0.033 mmol), or 3 (0.5 g, 0.032 mmol) to hexylamine (in 5 M excess) with toluene (10 mL). The mixture was then refluxed at 130 °C under nitrogen until the reaction was considered complete (by monitoring the disappearance of epoxide resonances at δ 2.7 and 3.1 in the ^{1}H NMR spectrum). The solvent and excess amine were removed in vacuo at 90 °C to give the final products: 4, 8, and 12 (from each respective siloxane backbone 1–3). Characterization for each siloxane is as follows.

Siloxane 4: clear oil, 87.2%; ^{1}H NMR δ 0.01 (s, $SiCH_3$), 0.50 (br, CH_2CH_2Si), 0.85 (t, $(CH_2)_5CH_3$), 1.25 (br, $CH_2(CH_2)_4CH_3$), 1.40 (br, $NHCH_2(CH_2)_4$), 1.50 (br, CH_2CH_2Si), 2.51 (br, $NHCH_2$-CH(OH)), 2.54 (br, $NHCH_2$), 3.39 (br, $Si(CH_2)_2CH_2OCH_2$), 3.47 (br, CH(OH)), 3.85 (br, CH(OH)); ^{13}C NMR δ 0.1 ($SiCH_3$), 13.0 ($(CH_2)_5CH_3$), 13.4 (CH_2CH_2Si), 23.2 (CH_2CH_2Si), 23.0–29.0 ($CH_2(CH_2)_4CH_3$), 32.0 ($NHCH_2(CH_2)_4$), 57.0 ($NHCH_2CH(OH)$), 67.8 (CH(OH)), 72.0 and 74.0 ($Si(CH_2)_2CH_2OCH_2$); FT-IR (cm^{-1}) ν 3400 (br), 2960 (s), 1600 (m), 1410 (m), 1260 (s), 1150 (m), 1100 (s). Anal. Calcd for $C_{28}H_{64}N_2Si_2O_5$: C, 59.52; H, 11.42; N, 4.96. Found: C, 60.29; H, 11.31; N, 4.90.

Siloxane 8: translucent oil, 93.0%; ^{1}H NMR δ 0.02 (s, $SiCH_3$), 0.48 (br, CH_2CH_2Si), 0.85 (t, $(CH_2)_5CH_3$), 1.26 (br, $CH_2(CH_2)_4$-CH_3), 1.40 (br, $NHCH_2(CH_2)_4$), 1.55 (br, CH_2CH_2Si), 2.51 (br, $NHCH_2CH(OH)$), 2.54 (br, $NHCH_2$), 3.40 (br, $Si(CH_2)_2CH_2$-OCH_2), 3.47 (br, CH(OH)), 3.90 (br, CH(OH)); ^{13}C NMR δ 0.1 ($SiCH_3$), 13.0 ($(CH_2)_5CH_3$), 13.4 (CH_2CH_2Si), 23.2 (CH_2CH_2Si), 23.0–29.0 ($CH_2(CH_2)_4CH_3$), 32.0 ($NHCH_2(CH_2)_4$), 57.0 ($NHCH_2$-CH(OH)), 68.7 (CH(OH)), 72.0 and 74.0 ($Si(CH_2)_2CH_2OCH_2$); FT-IR (cm^{-1}) ν 3400 (br), 2960 (s), 1600 (m), 1410 (m), 1260 (s), 1150 (m), 1100 (s).

Siloxane 12: opaque oil, 73.7%; ^{1}H NMR δ 0.01 (s, $SiCH_3$), 0.45 (br, CH_2CH_2Si), 0.82 (t, $(CH_2)_5CH_3$), 1.22 (br, $CH_2(CH_2)_4$-CH_3), 1.40 (br, $NHCH_2(CH_2)_4$), 1.50 (br, CH_2CH_2Si), 2.25 (br, $NHCH_2CH(OH)$), 2.50 (br, $NHCH_2$), 3.15 (br, $Si(CH_2)_2CH_2$-OCH_2), 3.35 (br, CH(OH)), 3.50 (br, CH(OH)); ^{13}C NMR δ 0.1 ($SiCH_3$), 13.4 (CH_2CH_2Si), 13.9 ($(CH_2)_5CH_3$), 22.2 (CH_2CH_2Si), 23.0–29.5 ($CH_2(CH_2)_4CH_3$), 31.5 ($NHCH_2(CH_2)_4$), 61.7 ($NHCH_2$-CH(OH)), 68.0 (CH(OH)), 7.15 and 74.5 ($Si(CH_2)_2CH_2OCH_2$); FT-IR (cm^{-1}) ν 3400 (br), 2960 (s), 1580 (m), 1410 (m), 1260 (s), 1150 (m), 1100 (s).

Preparation of Nonionic (Benzylamino)hydroxysiloxanes (5, 9, and 13). Into a two-necked flask was added one of the following siloxanes: 1 (0.4 g, 1.1 mmol), 2 (1.00 g, 5.58 mmol), or 3 (1.00 g, 1.5 mmol) to benzylamine (in 5 M excess) with toluene (10 mL). The mixture was then refluxed at 130 °C under nitrogen until the reaction was considered coplete (by monitoring the disappearance of epoxide resonances at δ 2.7 and 3.1 in the ^{1}H NMR spectrum). The solvent and excess amine were removed in vacuo at 90 °C to give the final products: 5, 9, and 13 (from each respective siloxane backbone 1–3). Characterization for each siloxane is as follows.

Siloxane 5: pale orange oil, 80.8%; ^{1}H NMR δ 0.1 (s, $SiCH_3$), 0.50 (br, CH_2CH_2Si), 1.60 (br, CH_2CH_2Si), 2.2 (s,$NHCH_2$), 3.40 (br, $Si(CH_2)_2CH_2OCH_2$), 3.70 (br, CH(OH)), 3.80 (br, $C_6H_5CH_2$), 3.90 (br, CH(OH)), 4.75 (br, $NHCH_2CH(OH)$), 7.25 (br, C_6H_5); ^{13}C NMR δ 0.1 ($SiCH_3$), 14.0 (CH_2CH_2Si), 23.0 (CH_2CH_2Si), 46.0 ($C_6H_5CH_2$), 64.0 ($NHCH_2CH(OH)$), 68.0 (CH(OH)), 7.25 and 74.0 ($Si(CH_2)_2CH_2OCH_2$), 128.0–132.0 (C_6H_5); FT-IR (cm^{-1}) ν 3400 (br), 3050 (s), 2960 (s), 1610 (s), 1550 (m), 1410 (m), 1260 (s), 1150 (m), 1100 (s). Anal. Calcd for $C_{30}H_{52}N_2Si_2O_5$: C, 62.45; H, 9.08; N, 4.85. Found: C, 65.51; H, 8.97; N, 5.67.

Siloxane 9: orange oil, 82.9%; ^{1}H NMR δ 0.1 (s, $SiCH_3$), 0.50 (br, CH_2CH_2Si), 1.60 (br, CH_2CH_2Si), 2.2 (s, $NHCH_2$), 3.30 (br, $Si(CH_2)_2CH_2OCH_2$), 3.70 (br, CH(OH)), 3.8 (br, $C_6H_5CH_2$), 3.90 (br, CH(OH)), 4.80 (br, $NHCH_2CH(OH)$), 7.25 (br, C_6H_5); ^{13}C NMR δ 0.1 ($SiCH_3$), 14.0 (CH_2CH_2Si), 23.5 (CH_2CH_2Si), 46.0 ($C_6H_5CH_2$), 64.0 ($NHCH_2CH(OH)$), 68.0 (CH(OH)), 72.5 and 74.0 ($Si(CH_2)_2CH_2OCH_2$), 128.0–132.0 (C_6H_5); FT-IR (cm^{-1}) ν 3400 (br), 3050 (s), 2960 (s), 1610 (s), 1550 (m), 1410 (m), 1260 (s), 1150 (m), 1100 (s);

Siloxane 13: pale yellow oil, 89.5%; ^{1}H NMR δ 0.1 (s, $SiCH_3$), 0.50 (br, CH_2CH_2Si), 1.60 (br, CH_2CH_2Si), 1.7 (s, $NHCH_2$), 3.40 (br, $Si(CH_2)_2CH_2OCH_2$), 3.70 (br, CH(OH)), 3.80 (br, $C_6H_5CH_2$), 3.90 (br, CH(OH)), 4.80 (br, $NHCH_2CH(OH)$), 7.25 (br, C_6H_5); ^{13}C NMR δ 0.1 ($SiCH_3$), 14.0 (CH_2CH_2Si), 23.5 (CH_2CH_2Si), 45.0 ($C_6H_5CH_2$), 64.4 ($NHCH_2CH(OH)$), 68.0 (CH(OH)), 72.5 and 74.0 ($Si(CH_2)_2CH_2OCH_2$), 128.0–132.0 (C_6H_5); FT-IR (cm^{-1}) ν 3400 (br), 3050 (s), 2960 (s), 1610 (s), 1550 (m), 1410 (m), 1260 (s), 1150 (m), 1100 (s).

Preparation of Nonionic (Methylamino)hydroxysiloxanes (6, 10, and 14). One of either siloxane 1 (0.2 g, 0.55 mol), siloxane 2 (1.00 g, 5.58 mmol), or siloxane 3 (1.00 g, 1.5 mmol) in toluene (10 mL) was mixed in a sample vial with a 5 M excess of methylamine and transferred into a glass tube (Pyrex with a length of 200 mm, outside diameter of 12.5 mm, wall thickness of 2 mm, with a constriction 30 mm long and 30 mm from the open end). The tube was sealed in vacuo and placed in a protective metal sheath (length of 400 mm, outside diameter of 25 mm, wall thickness of 2.5 mm, with screw tight ends) in an oven at 160 °C for 16 h. The sheath was then cooled to room temperature, the tube removed from the sheath, and the tip broken. The contents were poured into a round-bottomed flask, and the toluene and any excess reactants were removed in vacuo at 70 °C. The products 6, 10, and 14 from each respective siloxane backbone 1–3 were characterized by NMR and FT-IR.

Siloxane 6: colorless oil, 89.8%; ^{1}H NMR δ 0.1 (s, $SiCH_3$), 0.55 (br, CH_2CH_2Si), 1.65 (br, CH_2CH_2Si), 2.40 (s, $NHCH_3$), 2.45 (t, $NHCH_2CH(OH)$), 2.60 (br, $NHCH_3$), 3.45 (br, $Si(CH_2)_2CH_2$-OCH_2), 3.60 (br, CH(OH)), 3.90 (br, CH(OH)); ^{13}C NMR δ 0.1 ($SiCH_3$), 14.0 (CH_2CH_2Si), 23.2 (CH_2CH_2Si), 36.0 ($NHCH_3$), 58.0 ($NHCH_2CH(OH)$), 68.0 (CH(OH)), 72.5 and 73.8 ($Si(CH_2)_2$-CH_2OCH_2); FT-IR (cm^{-1}) ν 3400 (br), 2960 (s), 1610 (s), 1410 (m), 1260 (s), 1150 (m), 1100 (s). Anal. Calcd for $C_{18}H_{44}N_2Si_2O_5$: C, 50.90; H, 10.44; N, 6.59. Found: C, 52.05; H, 10.22; N, 4.55.

Siloxane 10: opaque white oil, 82.5%; ^{1}H NMR δ 0.1 (s, $SiCH_3$), 0.50 (br, CH_2CH_2Si), 1.60 (br, CH_2CH_2Si), 2.30 (s, $NHCH_3$), 2.70 (t, $NHCH_2CH(OH)$), 2.90 (br, $NHCH_3$), 3.30 (br, $Si(CH_2)_2CH_2$-OCH_2), 3.60 (br, CH(OH)), 4.00 (br, CH(OH)); ^{13}C NMR δ 0.1 ($SiCH_3$), 13.4 (CH_2CH_2Si), 23.2 (CH_2CH_2Si), 36.0 ($NHCH_3$), 58.0 ($NHCH_2CH(OH)$), 68.0 (CH(OH)), 72.0 and 73.0 ($Si(CH_2)_2$-CH_2OCH_2); FT-IR (cm^{-1}) ν 3400 (br), 2960 (s), 1600 (s), 1410 (m), 1260 (s), 1150 (m), 1100 (s).

Siloxane 14: white oil, 74.1%; ^{1}H NMR δ 0.1 (s, $SiCH_3$), 0.55 (br, CH_2CH_2Si), 1.60 (br, CH_2CH_2Si), 2.40 (s, $NHCH_3$), 2.70 (t, $NHCH_2CH(OH)$), 2.90 (br, $NHCH_3$), 3.40 (br, $Si(CH_2)_2CH_2$-OCH_2), 3.60 (br, CH(OH)), 3.90 (s, CH(OH)); ^{13}C NMR δ 0.1 ($SiCH_3$), 13.4 (CH_2CH_2Si), 23.2 (CH_2CH_2Si), 35.5 ($NHCH_3$), 58.0 ($NHCH_2CH(OH)$), 68.0 (CH(OH)), 72.5 and 73.9 ($Si(CH_2)_2$-CH_2OCH_2); FT-IR (cm^{-1}) ν 3400 (br), 2960 (s), 1640 (s), 1410 (m), 1260 (s), 1150 (m), 1100 (s).

Preparation of (Dicyclohexylamino)hydroxysiloxanes (7, 11, and 15). Into a two-necked flask was added one of the following siloxanes: 1 (0.5 g, 1.38 mmol), 2 (2.00 g, 11.17 mmol), or 3 (1.00 g, 1.50 mmol) to dicyclohexylamine (in 10% molar excess) with toluene (10 mL). The mixture was then refluxed at 140 °C under nitrogen until the reaction was considered complete (by monitoring the disappearance of epoxide resonances at δ 2.7 and 3.1 in the ^{1}H NMR spectrum). The solvent and excess amine were removed in vacuo at 90 °C to give the final products: 7, 11, and 15. The products 7, 11, and 15 from each respective siloxane backbone 1–3 were characterized by NMR and FT-IR as follows.

Siloxane 7: pale brown oil, 58.9%; ^{1}H NMR δ 0.1 (s, $SiCH_3$), 0.50 (br, CH_2CH_2Si), 0.80–1.60 (m (br), $C_6H_{11}N$), 1.60 (br, CH_2-CH_2Si), 2.50 (br, $NCH_2CH(OH)$), 2.60 (br, CH(OH)), 3.30 (br,

Table 1. Quantities and Yields for Cationic Aminosiloxane Synthesis (All Reactions Performed in Toluene Solvent at 0 °C Temperature with Reaction Times Held Constant at 1 h)

siloxane no.	reagent (mmol) siloxane	HBr	Tol (mL)	product no.	yield (%)	product appearance
4	1.89	9.48	10	16	77.0	brown oil
5	3.47	17.40	10	17	78.9	brown oil
6	0.98	4.90	5	18	84.8	brown oil
7	2.74	13.80	10	19	74.6	light brown oil
8	8.06	40.33	20	20	95.2	brown oil
9	2.48	12.50	10	21	84.5	brown oil
10	2.38	12.00	10	22	76.4	brown oil
11	1.54	7.70	10	23	89.7	light brown oil
12	0.65	3.25	5	24	75.9	brown oil
13	0.92	4.65	10	25	64.9	creamy oil
14	0.36	1.80	5	26	80.1	light brown oil
15	0.53	2.65	5	27	73.1	light brown oil

Table 2. Characteristic ^1H and ^{13}C NMR Resonances and FT-IR Absorbances for the Cationic Siloxanes As Prepared in Table 1[a]

siloxane no.	^1H NMR δ (ppm) A	B	C	^{13}C NMR δ (ppm) D	E	FT-IR (cm^{-1}) ν_{OH/NH_2^+}[b]	$\nu_{NH_2^+}$[c]
16	5.5	4.4	3.1	65.4	50.1	3406	1629
17	5.9	4.5	5.1	66.3	56.0	3408	1624
18	3.6	4.1	2.8	64.7	59.0	3450	1621
19	5.4	4.0	3.3	62.0	60.7	3403	1609
20	5.4	4.3	3.3	65.1	54.6	3411	1598
21	5.6	4.1	4.0	65.0	57.0	3419	1605
22	3.5	3.7	2.9	63.8	59.8	3452	1612
23	5.3	4.0	3.3	66.1	56.3	3404	1606
24	3.4	3.7	2.7	64.4	56.2	3259	1616
25	5.6	4.2	4.0	66.6	57.9	3457	1604
26	3.4	4.1	3.3	67.3	58.9	3455	1640
27	5.5	4.1	3.3	67.1	58.0	3404	1599

[a] Only resonances directly associated with the amine group are listed. [b] OH and NH_2^+ vibrations overlap and appear as a single broad peak. [c] N–H deformation of medium intensity.

$Si(CH_2)_2CH_2OCH_2$), 3.50 (s, $CH(OH)$); ^{13}C NMR δ 0.1 ($SiCH_3$), 14.0 (CH_2CH_2Si), 23.5 (CH_2CH_2Si), 25.4–33.0 ($C_6H_{11}N$), 57.9 ($NCH_2CH(OH)$), 66.2 ($CH(OH)$), 73.5 and 74.5 ($Si(CH_2)_2CH_2OCH_2$); FT-IR (cm^{-1}) ν 3400 (br), 2960 (s), 1610 (s), 1480 (s), 1260 (s), 1150 (m), 1100 (s). Anal. Calcd for $C_{40}H_{80}N_2Si_2O_5$: C, 66.24; H, 11.17; N, 3.86. Found: C, 65.05; H, 11.10; N, 5.02.

Siloxane 11: creamy oil, 49.0%; ^1H NMR δ 0.1 (s, $SiCH_3$), 0.50 (br, CH_2CH_2Si), 0.80–1.60 (m (br), $C_6H_{11}N$), 1.60 (br, CH_2CH_2Si), 2.40 (br, $NCH_2CH(OH)$), 2.60 (br, $CH(OH)$), 3.30 (br, $Si(CH_2)_2CH_2OCH_2$), 3.50 (s, $CH(OH)$); ^{13}C NMR δ 0.1 ($SiCH_3$) 14.0 (CH_2CH_2Si), 23.5 (CH_2CH_2Si), 25.4–33.3 ($C_6H_{11}N$), 57.3 ($NCH_2CH(OH)$), 66.2 ($CH(OH)$), 73.0 and 74.2 ($Si(CH_2)_2CH_2OCH_2$); FT-IR (cm^{-1}) ν 3400 (br), 2960 (s), 1610 (s), 1480 (s), 1260 (s), 1150 (m), 1100 (s).

Siloxane 15: brown oil, 63.1%; ^1H NMR δ 0.1 (s, $SiCH_3$), 0.50 (br, CH_2CH_2Si), 0.80–1.80 (m (br), $C_6H_{11}N$), 1.50 (br, CH_2CH_2Si), 2.30 (br, $NCH_2CH(OH)$), 2.70 (br, $CH(OH)$), 3.30 (br, $Si(CH_2)_2CH_2OCH_2$), 3.50 (s, $CH(OH)$); ^{13}C NMR δ 0.1 ($SiCH_3$), 14.0 (CH_2CH_2Si), 23.5 (CH_2CH_2Si), 25.4–33.0 ($C_6H_{11}N$), 56.5 ($NCH_2CH(OH)$), 67.0 ($CH(OH)$), 72.0 and 74.5 ($Si(CH_2)_2CH_2OCH_2$); FT-IR (cm^{-1}) ν 3400 (br), 2960 (s), 1610 (s), 1480 (s), 1260 (m), 1150 (m), 1100 (s).

Conversion of Nonionic to Cationic Aminohydroxysiloxanes. The reaction between the previously prepared aminohydroxysiloxanes, **4–15**, with a hydrogen bromide solution (48%, 0.715 g of HBr/mL of H_2O) in toluene proceeds smoothly at 0 °C to afford the cationic aminohydroxysiloxane compounds, **16–27** (Table 1). Reaction times were 1 h irrespective of the siloxane reagent. After removing the toluene, excess amine, and water in vacuo, the resultant products were analyzed by NMR and FT-IR (Table 2).

Results and Discussion

Aminosiloxanes have many applications, particularly in personal care products and also in the textile industry.

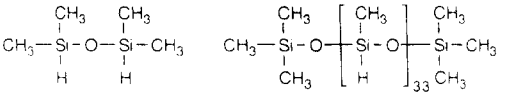


Figure 1. Tetramethyldisiloxane and poly(methylhydrogensiloxane).

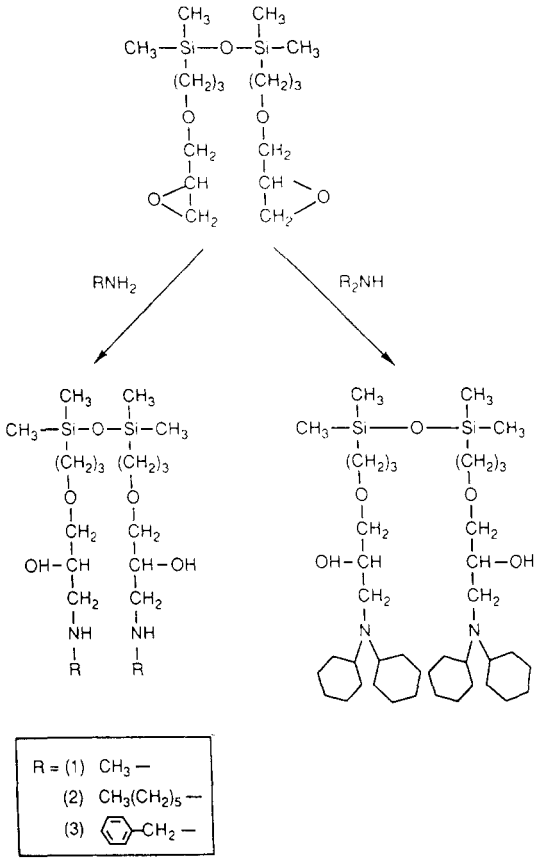
This is due largely to the reactivity of the hydrophilic amino group as opposed to the relatively inert hydrophobic siloxane backbone itself, making such polymers very useful surfactants. By extending epoxysilane chemistry to its epoxysiloxane counterpart, the synthesis of new surfactants, the aminohydroxysiloxanes, is possible through the reaction of amines in ring opening of epoxides. In this way, we have synthesized the novel cationic and nonionic siloxane surfactants containing both amino and hydroxy functional groups in high yields.

Kantor et al.[21] first prepared poly(methylhydrogensiloxane-*co*-dimethylsiloxane), $Me_3SiO[Me(H)SiO]_{23}[Me_2SiO]_{150}$, in 1954. We prepared this polymer by heating poly(methylhydrogensiloxane) (dp = 33), octamethylcyclotetrasiloxane, and hexamethyldisiloxane at 100 °C in the presence of acid-treated bentonite clay. The average molecular weight (M_w) of the final siloxane was 12 300 (gel permeation chromatography, GPC). In the ^1H NMR, the ratio of Si–Me protons to Si–H protons was 60:1, indicating a copolymer containing 150 Si–Me groups and 23 Si–H groups. The FT-IR shows characteristics of the Si–H absorption at ν = 2160 cm^{-1}.

To probe the versatility of the synthetic procedure, the reactivity of three different siloxanes was investigated. Tetramethyldisiloxane, having terminal Si–H groups, is the simplest siloxane used, and it is available as a commercial fine chemical. Chemical analysis could be used in this case to confirm the elemental composition of the final product. Such an analysis is meaningless with the other larger siloxanes, due to their polydispersity. Poly(methylhydrogensiloxane) (dp = 33; see Figure 1), having ~33 pendant Si–H groups along the siloxane backbone, was also available as a commercial sample. It was used to investigate the efficiency of replacing all the Si–H groups with firstly epoxide groups and subsequently with amino–hydroxy side groups. Finally, poly(methylhydrogensiloxane-*co*-dimethylsiloxane), $Me_3SiO[Me(H)SiO)]_{23}[Me_2SiO]_{150}$, was used to assess the reactivity of pendant Si–H groups surrounded by inert Me_2SiO groups in a larger, significantly more viscous, siloxane polymer.

All three siloxanes above were hydrosilylated with allyl glycidyl ether in the presence of a platinum catalyst to give the corresponding epoxysiloxanes **1–3** (see Scheme 1) in good yields. Characterization of the resultant epoxysiloxanes was based on ^1H and ^{13}C NMR and FT-IR.[22] The hydrosilylation reaction was monitored by observing the disappearance of the Si–H resonance in the ^1H NMR spectrum (δ 4.7) and the FT-IR spectrum (ν = 2160 cm^{-1}). The concomitant disappearance of resonances of the Si–H group and the allyl group of allyl glycidyl ether at δ 5.5 and 6.0 in the ^1H NMR, together with the appearance of resonances at δ 0.5 (CH_2CH_2Si), 1.5 (CH_2CH_2Si) and 3.4 ($CH_2OCH_2CH_2CH_2Si$), representative of the newly formed silylpropyl group, $(CH_2)_3Si$, clearly indicates the hydrosilylation reaction was successful for all three siloxanes. The pendant epoxide–siloxane resonances are at δ 2.6 (epoxy-CH_2) and δ 3.1 (epoxy-CH). ^{13}C NMR assignments were made for each of the three epoxysiloxanes, with the only major difference between these three siloxanes being the intensity of the methyl resonances on the silicon backbone at δ 0.01. The propyl group carbon resonances occurred at δ 13 ($CH_2CH_2CH_2Si$), 22 ($CH_2CH_2CH_2Si$), and

Scheme 2: General Reaction Scheme of 1° and 2° Amines to Siloxane 1



71 and 74 for the ether carbons ($CH_2OCH_2(CH_2)_2Si$). The epoxide carbons in the ^{13}C NMR spectrum were assigned to resonances at δ 46 and 51. The hydrosilylation reaction was also monitored by FT-IR where the disappearance of an absorption band at 2160 cm^{-1} (ν_{Si-H}) and at 1660 cm^{-1} ($\nu_{C=C}$) indicates completion of the reaction. The ν_{Si-H} absorption band is particularly sensitive as a measure of the course of the reaction. The strong band at 1260 cm^{-1} is due to $Si-CH_3$ vibration, while the ether C–O band occurs at 1150 cm^{-1} with the Si–O–Si band at 1100 cm^{-1}. The epoxide group is assigned[18] the sharp band at 910 cm^{-1}.

To the best of our knowledge, there have been no previous reports detailing the preparation of amino–hydroxy functional siloxanes. Our preparation, involving the ring-opening attack of epoxide groups by amines, proceeds, in most cases, quite smoothly, allowing high isolated yields. Amines are well-known accelerators[23] in curing epoxy resins through their ring-opening attack of the epoxy group. Therefore, hexylamine, benzylamine, methylamine, dicyclohexylamine, and triethylamine were all chosen to display a wide range of selectivity in both their functionality (e.g., primary, secondary, or tertiary) and structure (size and type of carbon chain attached to the amino group, e.g., aliphatic or aromatic chain or ring). The reaction of these various amines to the epoxysiloxanes is simply and efficiently achieved by anaerobically refluxing both components in an aromatic solvent for at least 16 h (see Scheme 2). The reaction requires the amine to have at least a bonded hydrogen atom to proceed. Tertiary amines will not react with the epoxy groups even under the most forcing conditions. This is in complete contrast to the work of Narracott[23] where tertiary amines do react with epoxy groups to form amino–hydroxy resins. It is useful then to consider the reaction of each amine in more detail.

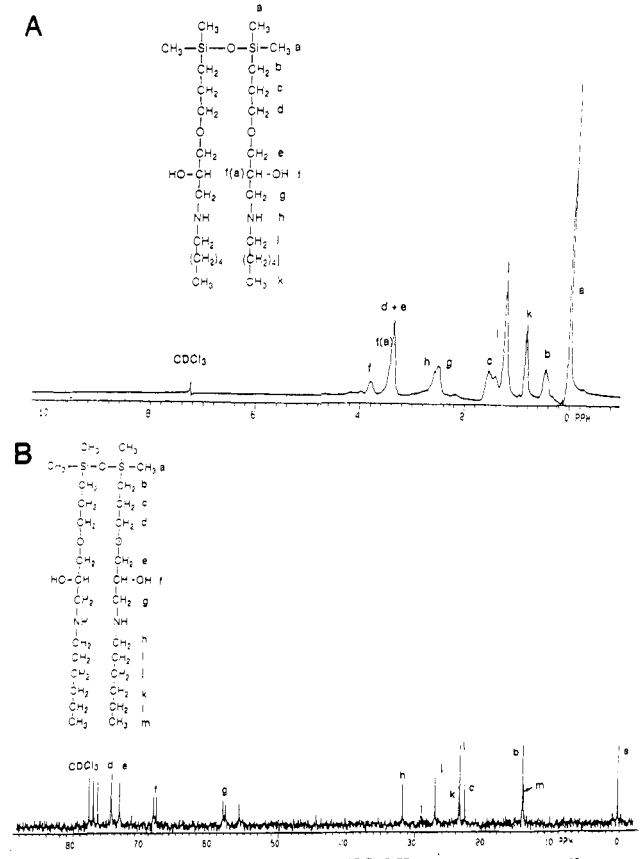


Figure 2. (A) ^1H NMR and (B) ^{13}C NMR spectra of siloxane **4**.

(Hexylamino)hydroxysiloxanes. All three epoxysiloxanes **1–3** were successfully reacted with hexylamine to give the respective products **4**, **8**, and **12**. So our attention will focus on the reaction of siloxane **4** only. The NMR and FT-IR spectra of siloxanes **8** and **12** are virtually identical. Addition of excess hexylamine (5 mol of amine to 1 mol of the epoxide group) to bis(glycidoxypropyl)-tetramethyldisiloxane at 130 °C gives the (hexylamino)-β-hydroxypropyltetramethyldisiloxane (**4**), a clear oil in high yield (87.2%). The completion of the reaction was confirmed by ^1H NMR where the epoxide ring resonances at δ 2.5 and 3.1 disappear, giving way to the appearance of hexylamine resonances at δ 0.9–1.8 consistent with ring opening of the epoxy groups by the hexylamine (Figure 1). FT-IR affirms the completion of the reaction through the disappearance of the epoxide band at 910 cm^{-1}, the subsequent formation of absorption bands at 3400 ($\nu_{O-H/N-H}$) and 1640 cm^{-1} (ν_{N-H} deformation), and the increase in intensity of aliphatic bands due to the hexyl chain at 2960 (ν_{CH}) and 1450 cm^{-1} (ν_{CH_2}). Assignment of the ^1H and ^{13}C NMR spectrum of siloxane **4** (Figure 2) was difficult to interpret precisely, and application of 2D NMR was necessary to accurately characterize the product. A COSY 2D NMR experiment was performed to elucidate nearest-neighbor coupling and to clearly define the assignment of all proton resonances (Figure 3). Starting from the unambiguously assigned resonance[21] of b at δ 0.5 and drawing the cross peaks immediately indicates the position of the methylene group, c at δ 1.5. There is now no difficulty in assigning the further resonances of the siloxane (see Figure 3). A HETCOR 2D NMR experiment was performed to show the correlation between the heteronuclear species, hydrogen, and carbon which allows the definitive assignment of all carbon resonances. The x-axis corresponds to the ^1H NMR spectrum, with the y-axis corresponding to the ^{13}C NMR spectrum (Figure 4). HETCOR was made use of to distinguish the hexyl

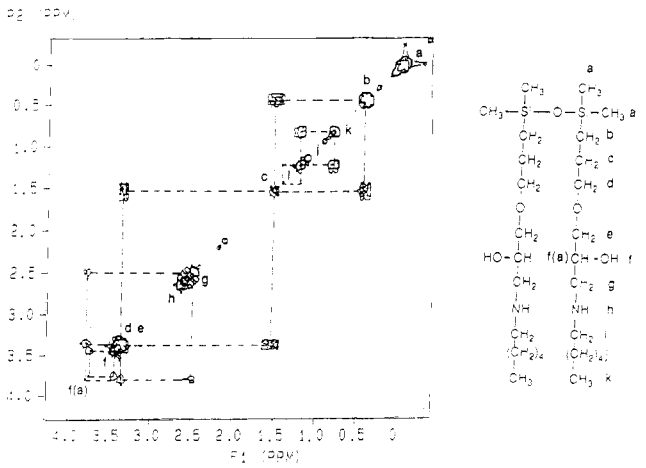


Figure 3. 2D COSY NMR spectrum of siloxane 4.

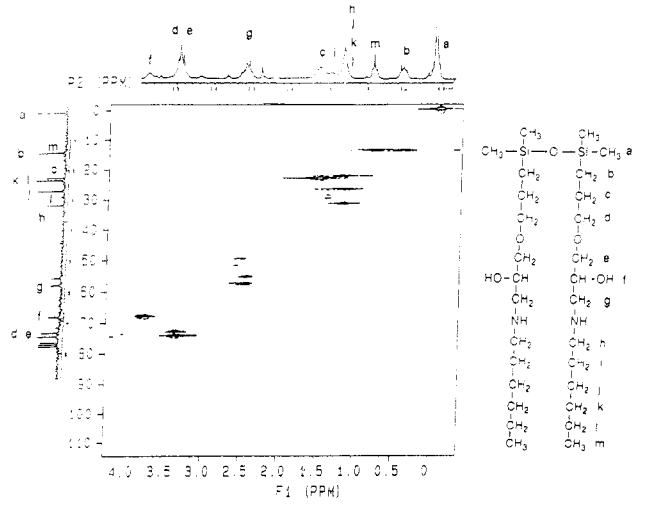


Figure 4. 2D HETCOR NMR spectrum of siloxane 4.

chain sequence and the position of the alcohol in the ^{1}H NMR spectrum. The hexyl cahin is split into three proton resonances: δ 0.7 ($NH(CH_2)_5CH_3$), δ 1.2 ($NHCH_2(CH_2)_4CH_3$), and δ 1.4 ($NHCH_2(CH_2)_4CH_3$). By drawing a dashed line from the proton resonances down to the contour peaks and following the line to the carbon resonances on the y-axis, it is possible to accurately assign all carbon resonances from their associated proton resonances. In this way, the hexyl chain has one carbon, m, at δ 14 (0.9 ppm in ^{1}H NMR), four carbons, l, k, j, and h, at δ 23, 23.5, 26, and 31 (1.2 ppm in ^{1}H NMR), and carbon i at δ 29 (1.4 ppm). The carbon with the attached hydroxyl group is easily identified as δ 68 in the ^{13}C NMR spectrum.

(Benzylamino)hydroxysiloxanes. All three epoxysiloxanes **1–3** were reacted with excess benzylamine at 130 °C for 16 h to give the pale yellow–orange oils **5**, **9**, and **13**, respectively, in high yields. The completion of the reaction was confirmed by ^{1}H NMR as the resonances associated with the epoxy group at δ 2.5 and 3.1 disappear, concomitant with the appearance of resonances due to the benzylamine group at δ 2.2 (CH_2NH), 3.8 ($C_6H_5CH_2$), and 7.2–7.4 (C_6H_5) (Figure 5). Complete identification of the (benzylamino)hydroxysiloxanes was again achieved by using COSY and HETCOR 2D NMR experiments. Starting from resonance b at δ 0.5 and connecting the cross peaks (indicative of coupling between adjacent groups) determines the position of the methylene group c at δ 1.5. Continuing such an analysis, the resonance at δ 3.3 must be due to both ether methylene groups, d and e, where d is coupled to c. The remaining methylene group e is coupled to the hydroxyl carbon f (δ 3.9), which in turn

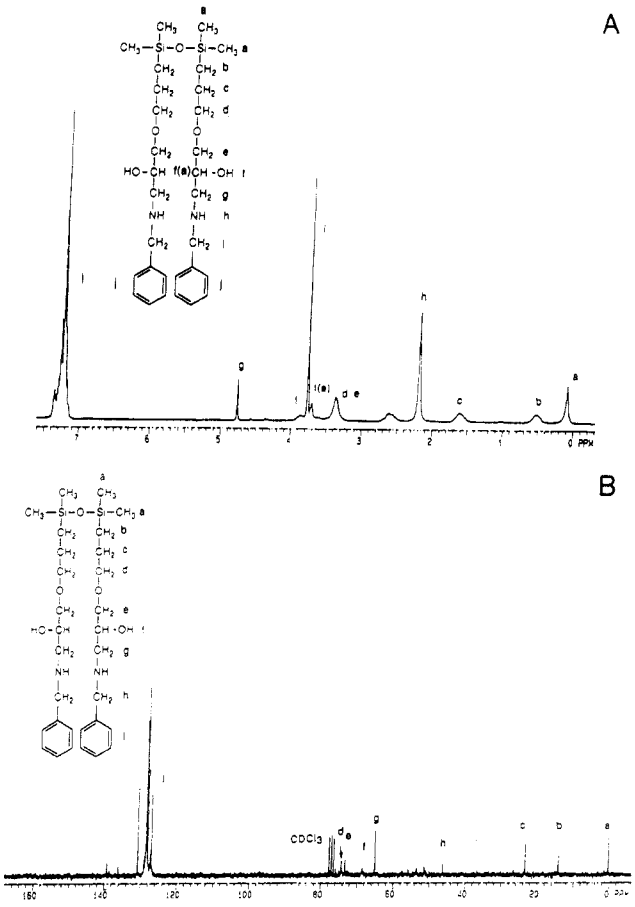


Figure 5. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of siloxane **5**.

is coupled to the methylene group g (δ 4.7). The nitrogen proton at δ 2.2 is then coupled to both methylene groups, g (above) and i (δ 3.8), the latter being coupled to the benzyl ring at δ 7.2. The COSY experiment is essential for distinguishing between resonances at δ 3.8 (i) and 4.8 (g). The HETCOR experiment can then again be used to accurately assign all carbon resonances from their respective proton resonances. FT-IR studies further affirm that the reaction has gone to completion with the absence of the epoxide band at 910 cm^{-1}. In addition, absorption bands can clearly be seen at 1660 ($\nu_{C=C}$), 3050 ($\nu_{aromatic\ CH}$), and 3400 cm^{-1} ($\nu_{NH/OH}$). The presence of two sharp absorption bands at 695 and 752 cm^{-1} indicates that the benzene ring is monosubstituted, so that no other additional substitution has taken place on the aromatic ring during the reaction.

(Methylamino)hydroxysiloxanes. All three epoxysiloxanes **1–3** were reacted with excess methylamine at 160 °C for 16 h to give the products **6**, **10**, and **14**, respectively. For example, methylamine, siloxane **1**, and toluene were placed in a sealed glass tube and heated at 160 °C for 16 h. As the boiling points of both reagents are exceeded in such a reaction, pressure builds within the sealed glass tube. For this reason, thick-walled glass was used and the sealed reaction vessel was placed inside a protective metal jacket before heating. Interestingly, there is no reaction below 130 °C. On cooling the reaction tube to room temperature, the resultant product was placed into a round-bottomed flask, and the solvent and any excess amine were removed in vacuo to give a clear oil, siloxane **6**. The product was characterized by ^{1}H, ^{13}C, and 2D NMR and FT-IR. The ^{1}H NMR spectrum (see Figure 6) clearly shows the assignments for all protons as analyzed (*vide supra*) by 2D COSY NMR. The nitrogen proton, h, appears at δ 2.7 near the methyl resonance, i, of the amine

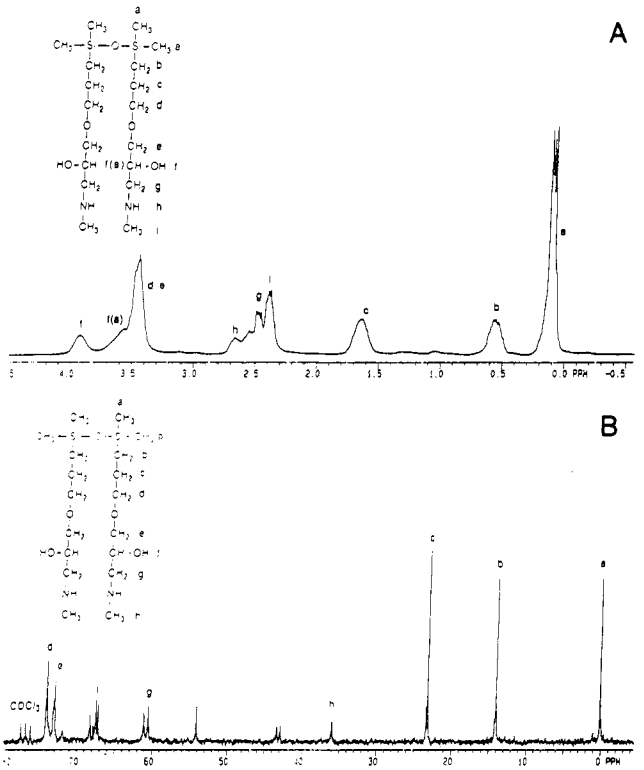


Figure 6. (A) ^1H NMR and (B) ^{13}C NMR spectra of siloxane **6**.

at δ 2.4. The ^{13}C NMR spectrum (see Figure 6) was unequivocally assigned by information obtained from the ^1H NMR, COSY, and HETCOR 2D NMR spectra. In this way, the methyl resonance of the methylamine group appears at δ 36. The methylamine is the smallest of the amines used in these reactions, and its products the three (methylamino)hydroxysiloxanes **6**, **10**, and **14** are free-flowing, low-viscosity oils unlike their viscous, more sterically hindered (hexylamino)- and (benzylamino)-hydroxysiloxane counterparts. Increasing the steric bulk of the side chain dramatically increases the product viscosity.

(Dicyclohexylamino)hydroxysiloxanes. All three epoxysiloxanes **1–3** were reacted with a 10% molar excess of dicyclohexylamine, a secondary amine with two bulky aliphatic cyclohexyl rings, at 130 °C for 48 h, to give the products **7**, **11**, and **15**. The reaction was monitored by ^1H NMR and was considered complete when the epoxide group resonances at δ 2.6 or 3.1 disappeared. The complex pattern of resonances at δ 0.8–1.8 (in the ^1H NMR; see Figure 7) and at 25–32 (in the ^{13}C NMR; see Figure 7) are due solely to the large aliphatic cyclohexyl groups. Complete spectral assignment of the product NMR resonances, however, could still be accomplished with COSY and HETCOR 2D NMR. For instance, the resonance h in the ^1H (δ 1.8) and ^{13}C (δ 48) spectra is assigned to the NC–*H* and N*C*–H, respectively, of the cyclohexylamine.

The tertiary amine, triethylamine, did not react (even under forcing conditions) with the epoxy groups, and this is believed to be a consequence of the amine having no active hydrogen with which to partake in the ring-opening reaction.

Cationic Aminohydroxysiloxanes. It was decided to test the stability of the poly(dimethylsiloxane) with amines in the presence of hydrogen bromide, a strong acid capable of breaking down the siloxane backbone. The addition of hydrogen bromide (48%, 0.715 g of HBr/mL of H_2O) to poly(dimethylsiloxane) in toluene at 0 °C does

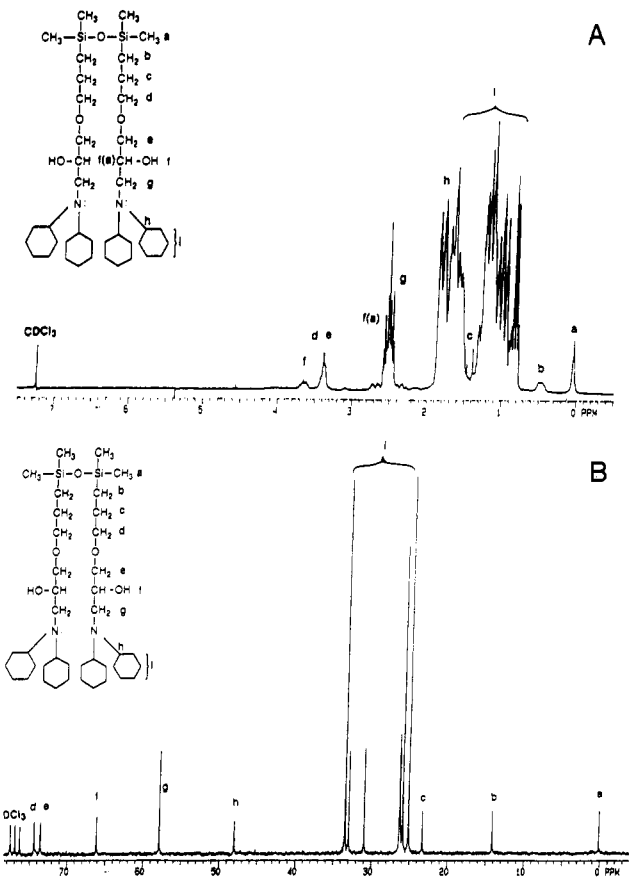


Figure 7. (A) ^1H NMR and (B) ^{13}C NMR spectra of siloxane **7**.

in fact break down the siloxane backbone, resulting in a complex mixture of reaction products (confirmed by GPC). We believe that hydrogen bromide will preferentially attack the nitrogen present in the side chains and therefore not attack the siloxane structure. To determine whether the amino group rather than the siloxane backbone is preferred in the reaction with hydrogen bromide, amine was added to poly(dimethylsiloxane) in toluene and cooled to 0 °C. Hydrogen bromide in equimolar amount was then slowly added and left to stir for 1 h. The mixture was extracted with water (3 × 10 mL) and the organic layer subsequently dried over magnesium sulfate and filtered. The toluene was removed in vacuo, giving a clear oil which was characterized by NMR and GPC. GPC confirmed the integrity of the original siloxane backbone, indicating the preference of hydrogen bromide attack onto the nitrogen-containing amine. Proton NMR on the aqueous layer confirmed the formation of amine salt. Note that it is not recommended that either the cationic aminosiloxanes or even the neutral aminosiloxanes be introduced into a GPC column. Experience shows that irreversible column breakage occurs.

Cationic aminohydroxysiloxane surfactants were prepared by simply adding excess hydrogen bromide solution to the nonionic siloxanes **4–15** to give the corresponding cationic aminosiloxanes **16–27** in good yields (see Scheme 3). FT-IR was used to monitor the formation of the products (see Figure 8). The large absorption band at 3400 cm^{-1} is due to the hydroxyl and cationic nitrogen, and the band between 1600 and 1650 cm^{-1} is due to NH_2^+ deformation. The intensity of the C–H band at approximately 2950 cm^{-1} is governed by the number of CH groups in the compound (the C–H band is sometimes partially obscured by the presence of the large salt $NH_2^+Br^-$ absorption band). The (methylamino)siloxane **18** shows a very slight C–H stretching band, due in part to its weaker

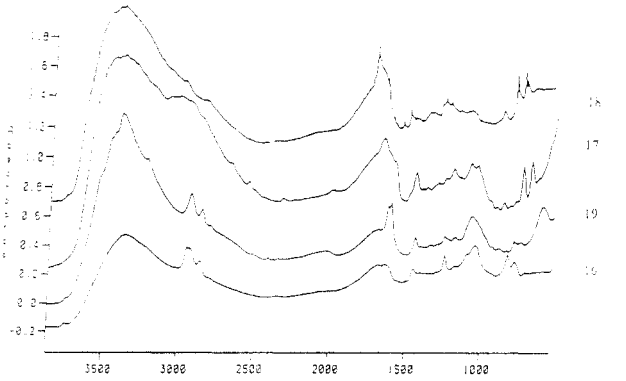
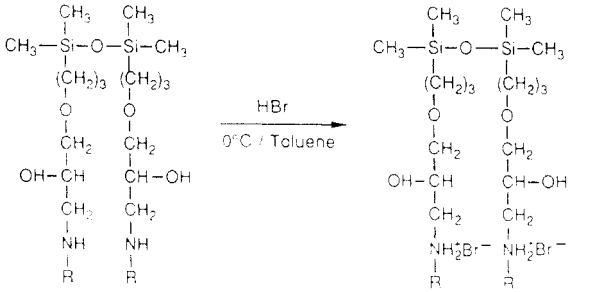


Figure 8. FT-IR spectra of siloxanes **16–19** (hexylamine, benzylamine, methylamine, and dicyclohexylamine analogs of siloxane **1** after treatment with HBr).

Scheme 3. Conversion of Nonionic to Cationic Siloxanes



intensity and also the overlap of the $NH_2^+Br^-$ salt band. It is also possible to identify the C–H band for the (hexylamino)- and (dicyclohexylamino)siloxanes **16** and **19**. The (benzylamino)siloxane **17** clearly indicates the presence of aromatic CH at $\nu = 3050\ cm^{-1}$. The cationic aminohydroxysiloxanes were further characterized by ^1H and ^{13}C NMR (see Figure 9) in conjunction with 2D NMR (all spectra were run in DMSO-d_6). The protonated nitrogen resonance of siloxane **16** is located downfield at δ 5.0 in the ^1H NMR spectrum (see Figure 9 and Table 2) representing a considerable difference over its nonionic counterpart, siloxane **4**, where the N–H proton resonance occurs at δ 2.6. The difference results from the extra acidity associated with cationic NH_2^+ protons, and the associated electron-withdrawing effect of the electronegative bromine atom. Furthermore, Figure 9 shows that the ionic $NH_2^+Br^-$ group imparts a similar, though smaller, change in chemical shift to neighboring hydrogen atoms. Comparing ^1H NMR spectra (see Figures 2 and 5), the neighboring methylene proton resonances, g, have shifted from δ 2.5 (see Figure 2) to 3.1 ppm (see Figure 5); likewise the alcohol proton resonance, f, has shifted from δ 3.9 to 4.5, and the first methylene protons of the hexyl group, i, have also shifted slightly from δ 1.7 to 1.9.

Summary

Aminosiloxanes are a relatively new class of polymers that couple the unique properties of hydrophobic poly(dimethylsiloxanes) with the reactivity of the hydrophilic amino groups. Both nonionic and cationic aminosiloxanes form the basis for a rapidly developing and diverse field of applied chemistry, particularly in their role as surfactants in the personal care industry. A new, simple, yet efficient synthesis, of aminohydroxysiloxanes was accomplished by initial hydrosilylation to form epoxysiloxanes, followed by ring opening of the epoxy group with various substituted amines. Five amines were systematically studied: methylamine, hexylamine, benzylamine, dicyclohexylamine, and triethylamine. The tertiary amine,

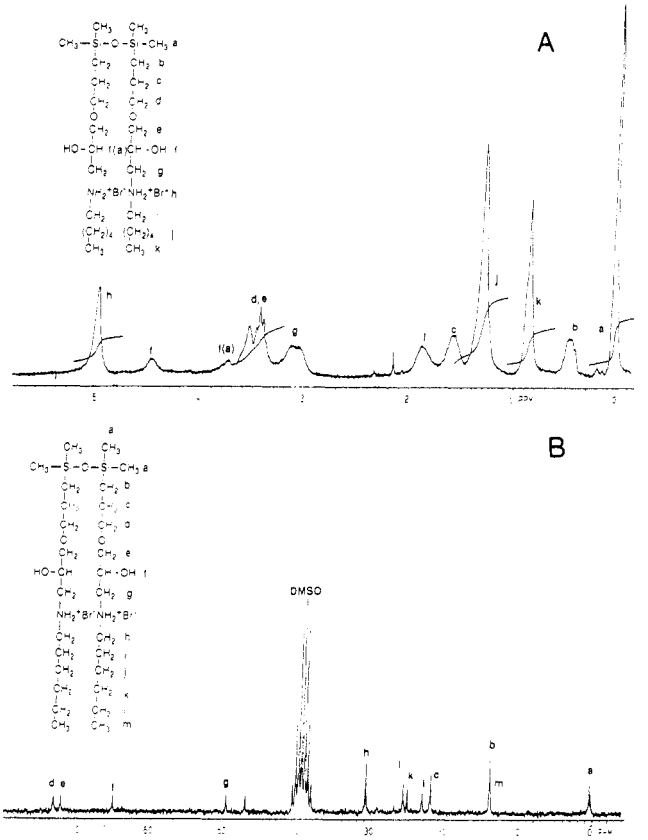


Figure 9. (A) ^1H NMR and (B) ^{13}C NMR spectra of siloxane **16**.

triethylamine, did not react with the epoxysiloxane, as there are no available protons for epoxy ring opening. The remaining nonionic aminohydroxysiloxanes were prepared in good yields and were fully characterized by FT-IR and NMR (^1H, ^{13}C, and 2D). Two-dimensional NMR, in particular, COSY and HETCOR pulse sequences, were successfully applied to the siloxane aminohydroxyglycidylpropyl side chains to permit unequivocal and complete spectral assignments.

The cationic aminohydroxysiloxanes were subsequently synthesized in high yield by reacting the nonionic siloxanes with a hydrogen bromide solution. The structure of the cationic amino side chains on the siloxane backbone could be similarly characterized using NMR (^1H, ^{13}C, and 2D) and FT-IR. The reaction can be monitored by the appearance of a large peak in the ^1H NMR spectrum due to the NH_2^+ resonance (δ 4.0–5.0) and the concomitant disappearance of the NH resonance associated with the nonionic siloxane counterparts (at approximately δ 2.5).

Today's surfactant chemists must consider molecular parameters, such as surface orientation, steric effects, and functionality in tandem with traditionally recognized surface-active properties. Adsorption of polymeric surfactants on particles is already very important to the understanding of dispersion stability and flotation of particles.[24,25] Surface studies of adsorbed surfactants have received considerable interest recently because of their potential use in enhanced oil recovery, in drug production, and in cosmetic formulations.[26,27] Investigations on the adsorption of both the aminohydroxysiloxanes and their cationic derivatives onto SiO_2 surfaces are therefore already in progress and will be the subject of a forthcoming paper.

Conclusion

Novel siloxane polymers containing amino and hydroxy functional groups have been synthesized, isolated in high

yields, and characterized for the first time. Cationic amino–hydroxy functional siloxanes are easy to prepare, undergoing protonation at the nitrogen atom (in place of the hydroxy group) to give resultant products also in high yields. These novel siloxane products form a new generation of siloxane surfactants whose properties are now undergoing further investigation.

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Supplementary Material Available: FT-IR spectra of siloxanes 1, 4, and 7 and NMR spectra of siloxane 1 (5 pages). Ordering information is given on any current masthead page.

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