Synthesis of Surface-Active Quaternary Amino Polyfluorosiloxanes

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ABSTRACT: We report synthesis of surface-active quaternary amino polyfluorosiloxanes. Hydrosilation of silanic hydrogen containing polyfluorosiloxanes with olefinic epoxides, in the presence of a platinum–divinyltetramethyldisiloxane complex gave epoxy polyfluorosiloxanes. These, on further reaction with various amines followed by quaternization, gave quaternary amino polyfluorosiloxanes. The quaternary amino polyfluorosiloxanes reduce surface tension of water to 25 mN/m^2 at a 25-millimolar concentration. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1700–1708, 2000

Key words: synthesis; fluoro; fluorosiloxanes; quaternary; surface-active

INTRODUCTION

Synthesis of quaternary aminosiloxanes has received considerable attention due to their widespread application such as surface-active agents,[1]
fire fighting agents,[2] bactericide, anticariogenic agents,[3,4] skin conditioning agents,[5] etc. In the aqueous medium, the hydrophilic quaternary ammonium portion of these molecules is pulled into the solution, where as the hydrophobic polysiloxane chain is attracted toward the air–water interface, resulting in the lowering of surface tension of water. Fluorine containing quaternary amino compounds also show excellent surface activity.[6–8]

Fluoropolymers and siloxane polymers have very low surface energies, in addition to useful properties like chemical and biological inertness, low dielectric constants, low coefficient of friction[9] etc. Resistance to attack by biological systems makes these polymers useful in marine coatings.[10] Incorporation of hydrophobic fluorocarbon groups and hydrophilic quaternary ammonium group in the flexible siloxane backbone would result in quaternary amino fluorosiloxane surfactants with excellent surface-active properties.

Quaternary fluorosilicone was used as oil repellent agent and dispersing agent.[11] It was prepared by reacting $CF_3(CF_2)_6CONH(CH_2)_3NMe_2$ with $ClCH_2CH_2CH_2Si(OMe)_3$. Quaternary amino fluorocarbons are generally prepared by quaternization of fluorocarbon amines using alkyl halide. Quaternary fluorocarbon[7] $(CF_3)_2CF(CF_2)_6CH_2$-$CH(OH)$-CH_2-$N^+Me_3\ I^-$ were reported to be synthesized by reaction of $(CF_3)_2CF(CF_2)_6CH_2$-$CH(OH)$-CH_2-NMe_2 with methyl iodide. Synthesis of surface-active polyfluorosiloxanes containing pendent fluoroalkyl and quaternary amino groups has not been reported.

In this work, quaternary amino polyfluorosiloxanes were synthesized by reaction of various silanic hydrogen containing polyfluorosiloxanes with allyl glycidyl ether in the presence of a platinum–divinyltetramethyldisiloxane complex, followed by reaction with amines and finally, quaternization. Silanic hydrogen terminated poly (3,3,3-trifluoropropyl, methyl-*co*-dimethyl) siloxanes were synthesized by ring opening copolymer-

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Table I

Ex.	D_3 g	TFPMS g	BuLi Mol	Time (hs)/ Temp °C	Molecular Weight by ^{1}H-NMR	% Yield
a	11	10	0.0125	24/0°C	1796	93%
b	11	10	0.005	36/0°C	4316	91%
c	11	10	0.0025	36/0°C	8516	91%

ization of hexamethylcyclotrisiloxane and 1,3,5-tris(3,3,3-trifluoropropyl), 1,3,5-trimethyl cyclotrisiloxane using butyllithium, followed by termination with chlorodimethylsilane. Alternatively, silanic hydrogen containing fluorocyclosiloxanes were obtained by cohydrolysis of dichloromethylsilane and 3,3,3 trifluoropropyl, methyl dichlorosilane. This fluorocyclosiloxane further undergoes ring-opening polymerization using butyllithium to give silanic hydrogen containing linear polyfluorosiloxanes. The quaternary amino polyfluorosiloxane obtained from above silanic hydrogen polyfluorosiloxane were found to be excellent surface active as well as antimicrobial agent.

EXPERIMENTAL

Methods

FTIR spectra were recorded on Polaris™ FTIR spectrometer (Mattson Instrument) using NaCl crystal in the infrared region of 400–4000 cm^{-1}. NMR spectra were recorded on Bruker ACP 360 MHz spectrometer using $CDCl_3$ as a solvent. Chemical shifts of various peaks in the spectra were reference with respect to $CHCl_3$ peak appearing at 7.26 in $CDCl_3$. Solution of quaternary aminopolyfluorosiloxane were prepared in distilled water in the concentration ranging from 0.1 to 100 mM. The surface tension was measured at 25°C by drop method. The flow rate of water was 0.025 mL per min.

Chemicals

Hexamethylcyclotrisiloxane (D3), (Gelest, 97%); 1,3,5-tris(3,3,3-trifluoropropyl)-1,3,5-trimethyl cyclotrisiloxane (TFPMS), (Gelest, 95%); 3,3,3-trifluoropropyl, methyl dichlorosilane, (Gelest, 98%); dichloromethylsilane, (Gelest, 98%); butyllithium solution, (Aldrich, 2.5 M solution in hexane);
chlorodimethylsilane, $HSiMe_2Cl$, (Gelest, 98%); trifluoromethanesulfonic acid, (Aldrich, 99%); platinum-divinyltetramethyldisiloxane complex (Gelest, 3-3.5% of platinum concentration. The solution of 5 g of catalyst in 25 mL toluene was used for hydosilation reaction.); THF, (dried over sodium metal using benzophonone indicator); toluene, (dried over sodium metal); allyl glycidyl ether, (Lancaster, 97%,); allylamine, (Lancaster, 98%); methyliodide (SISCO Research Lab. 99%,).

Reaction Procedures

Synthesis of Silanic Hydrogen-Terminated Poly(3,3,3 trifluoropropyl, methyl-co-dimethyl)siloxane Copolymer (1)

Butyllithium (BuLi) (0.0125 mol) in *n*-hexane was taken in dry three-necked round-bottom flask containing 60 mL of dry THF at 0°C under an inert atmosphere of nitrogen. A solution of 10g hexamethylcyclotrisiloxane (D_3) and 10g of 1,3,5-tris(3,3,3 trifluoropropyl), 1,3,5-trimethyl cyclotrisiloxane (TFPMS), in 40 mL of dry THF was injected dropwise into the flask containing the BuLi/THF solution. The reaction mixture was gently stirred at 15°C for 40 hs under nitrogen atmosphere. The living polymer was then terminated by addition of an excess of chlorodimethylsilane (HMe_2SiCl). Unreacted chlorosilane and the solvent were distilled off under vacuum at 35°C and the LiCl precipitate was filtered off. The product was washed with 25 mL water to remove last traces of LiCl precipitate. The monofunctional silanic hydrogen terminated poly(3,3,3 trifluoropropyl, methyl-co-dimethyl) siloxane was then characterized using FTIR and ^{1}H-NMR. Control in the molecular weight was achieved by varying the butyllithium concentrations. Table I shows percentage yield and molecular weight obtained at different concentrations of butyllithium.

Product Characteristics. Clear, transparent liquid, FTIR peak due to Si—H at 2115 cm^{-1}, Si-CH_3 at 1260 cm^{-1}, —Si—O—Si— at 1186 cm^{-1}; ^{1}H-NMR ($CDCl_3$) peaks at δ 0.089 (s, —Si(C$\mathbf{H}_3$)$_2$), 0.171(s, —SiHC$\mathbf{H}_3$), 0.5 (t, —C$\mathbf{H}_2$Si), 0.74 (t,

$CF_3CH_2C\mathbf{H}_2$—Si—), 0.86 (t, —$C\mathbf{H}_3$), 1.28 (m, —$C\mathbf{H}_2$—), 2.04 (t, —$C\mathbf{H}_2$—CF3) and 4.68 (s, —Si—**H**).

Synthesis of Silanic Hydrogen Containing Polyfluorosiloxane (2)

Synthesis of Silanic Hydrogen Containing Fluorocyclosiloxanes. 3,3,3 Trifluoropropyl, methyldichlorosilane, and dichloromethylsilane (in a 1 : 1 molar ratio) were added dropwise to 500 mL ether : water system. The temperature of the reaction mixture was maintained at 0°C during the addition of dichlorosilanes. After the hydrolysis, the acidic aqueous layer was removed and the organic layer was washed with 200 mL water each time until neutral pH. The organic layer containing mixture of fluorocyclosiloxane and high molecular weight polymer was dried over anhydrous sodium sulfate, and ether was distilled off under vacuum. The fluorocyclosiloxane was distilled under vacuum (10 mm) 140°C and characterized using FTIR and ^{1}H-NMR.

Product Characteristics. Clear, transparent liquid (obtained at 140°C), FTIR peak due to Si—H at 2115 cm^{-1}, Si—CH_3 at 1260 cm^{-1}, —Si—O—Si at 1186 cm^{-1}; ^{1}H-NMR ($CDCl_3$) peaks at δ 0.08 (s, $SiC\mathbf{H}_3$), 0.17 (s, $Si(C\mathbf{H}_3)H$), 0.74 (t, $CF_3CH_2C\mathbf{H}_2$—Si—), 2.04 (t, —$C\mathbf{H}_2$—CF3)and 4.68 (s, Si—**H**). The molecular weight calculated using ^{1}H-NMR was found to be 432.

Butyllithium (BuLi) (0.012 mol) in *n*-hexane was taken in a three-necked flask containing 40 mL of dry THF at 0°C under an inert atmosphere of nitrogen. A solution of 10 g silanic hydrogen containing fluorocyclosiloxane in 40 mL dry THF was injected into the flask containing BuLi/THF solution. The reaction mixture was stirred at 15°C for 15–40 h under nitrogen atmosphere. The living polymer was then terminated by addition of an excess of chlorodimethylsilane (HMe_2SiCl). The unreacted chlorosilane and the solvent were distilled off under vacuum at 35°C and LiCl precipitate was filtered off. The product was washed with 25 mL water each time to remove last traces of LiCl particles. The silanic hydrogen containing polyfluorosiloxane was then characterized using FTIR and ^{1}H-NMR. The molecular weight calculated using ^{1}H-NMR was found to be 3836.

Product Characteristics. Clear, transparent liquid, FTIR peak due to Si—H at 2115 cm^{-1}, Si—CH_3 at 1260 cm^{-1}, —Si—O—Si at 1186 cm^{-1}; ^{1}H-NMR ($CDCl_3$) peaks at δ 0.089 (s, $Si(C\mathbf{H}_3)_2$), 0.171(s, $SiHC\mathbf{H}_3$), 0.5 (s, —$C\mathbf{H}_2Si$), 0.74 (t, $CF_3CH_2C\mathbf{H}_2$—Si—), 0.86 (t, —$C\mathbf{H}_3$), 1.28 (m, —$C\mathbf{H}_2$—), 2.04 (t, —$C\mathbf{H}_2$—CF3) and 4.68 (s, Si—**H**).

Synthesis of Silanic Hydrogan Containing Poly[(3,3,3-trifluoropyl, methyl)-co-(dimethyl)] Siloxane Polymer (3)

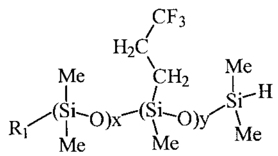
Silanic hydrogen (10 g) containing fluorocyclosiloxane, 5 g hexamethylcyclotrisiloxane, 1 g hexamethyldisiloxane, and trifluoromethanesulfonic (0.5 g) acid were stirred at 25°C for 10 h under the inert atmosphere of nitrogen. The product was dissolved in 50 mL of chloroform and the organic layer was washed with 50 mL of water each time, until neutral pH. The organic layer was dried over sodium sulfate and the solvent was distilled off under vacuum. The product was characterized using FTIR and ^{1}H-NMR.

Product Characteristics. Colorless, viscous liquid, FTIR peak due to Si—H at 2115 cm^{-1}, Si—CH_3 at 1260 cm^{-1}, —Si—O—Si at 1186 cm^{-1}; ^{1}H-NMR ($CDCl_3$) peaks at δ 0.08 (s, $SiC\mathbf{H}_3$), 0.17 (s, $Si(C\mathbf{H}_3)H$), 0.74 (t, $CF_3CH_2C\mathbf{H}_2$—Si—), 2.04 (t, —$C\mathbf{H}_2$—CF3) and 4.68 (s, Si—**H**).

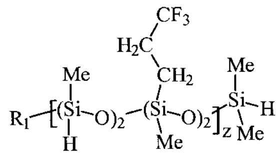
Synthesis of Epoxy Polyfluorosiloxane (4,5,6)

Allyl glycidyl ether (AGE) (5 g) and 0.2 mL solution of platinum–divinyl tetramethyldisiloxane complex were taken in a two-necked round-bottom flask under the inert atmosphere of nitrogen. The solution of 2 g silanic hydrogen containing polyfluorosiloxane (1,2 or 3) in 15 mL dry toluene was added dropwise to allyl glycidyl ether–platinum mixture and the reaction mixture was stirred at 25°C until disappearance of FTIR resonance frequency due to Si—H at 2115 cm^{-1}. Toluene and excess AGE were distilled off under vacuum. The respective epoxy polyfluorosiloxanes (4,5 or 6) thus obtained were characterized using FTIR and ^{1}H-NMR.

Product Characteristics. Siloxane (4,5): clear, transparent viscous oil, 88% yield, FTIR resonance frequency due to Si—CH_3 at 1260 cm^{-1}, —Si—O—Si at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR ($CDCl_3$) peaks at δ (ppm) 0.1(s, $SiC\mathbf{H}_3$), 0.5 (t, —$C\mathbf{H}_2Si$), 0.74 (t, $CF_3CH_2C\mathbf{H}_2$—Si—), 0.86 (t, —$C\mathbf{H}_3$, t), 1.28 (m, —$C\mathbf{H}_2$—), 1.57 (m, —$C\mathbf{H}_2CH_2Si$—), 2.04 (t, —$C\mathbf{H}_2$—CF_3), 2.6–2.7 (d,



(1)



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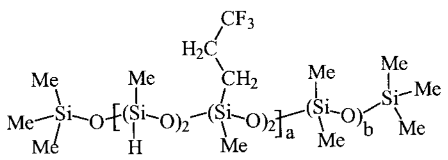

(3)

Figure 1 Silanic hydrogen containing polyfluorosiloxanes.

epoxy —C**H**$_2$), 3.13 (m, epoxy —C**H**), 3.4–3.6 (m, —(C**H**$_2$OC**H**$_2$ (CH$_2$)$_2$Si).

Siloxane (6): clear, transparent viscous oil, 88% yield, FTIR resonance frequency due to Si—CH$_3$ at 1260 cm^{-1}, —Si—O—Si at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR peaks at δ (ppm) 0.1(s, SiC**H**$_3$), 0.5 (t, —C**H**$_2$Si), 0.74 (t, CF$_3$CH$_2$C**H**$_2$—Si—), 1.57 (m, —C**H**$_2$CH$_2$Si—), 2.04 (t, —C**H**$_2$—CF3), 2.6–2.7(d, epoxy —C**H**$_2$), 3.13 (m, epoxy —C**H**), 3.4–3.6 (m, —(C**H**$_2$OC**H**$_2$ (CH$_2$)$_2$Si).

Synthesis of Olefinic Aminohydroxypoly Fluorosiloxanes (7,8,9)

A solution of 2 g of epoxy polyfluorosiloxane (4,5 or 6) in 10 mL toluene was taken in a three-necked dry round-bottom flask attached with reflux condenser. Allylamine (5 g) was added to it, and the reaction mixture was refluxed at 80°C for 7 h under nitrogen atmosphere. Excess allylamine and toluene were distilled off and the respective amino hydroxy polyfluorosiloxane (7,8 or 9) thus obtained was characterized by FTIR, ^{1}H-NMR.

Product Characteristics. Siloxane (7,8): clear, transparent viscous oil, 88% yield, FTIR resonance frequency due to Si—CH$_3$ at 1260 cm^{-1}, —Si—O—Si at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR (CHCl$_3$) peaks at (ppm) 0.1(s, SiC**H**$_3$), 0.5 (t, —C**H**$_2$Si), 0.74 (t, CF$_3$CH$_2$C**H**$_2$—Si—), 0.86 (t, —C**H**$_3$), 1.28 (m, —C**H**$_2$—), 1.57 (m, —C**H**$_2$CH$_2$Si—), 2.04 (t, —C**H**$_2$—CF3), 2.58 (m, CH(OH)—C**H**$_2$—NH, CH$_2$=CH—C**H**$_2$NH), 3.85 (m, —C**H**(OH)), 5.17 (m, C**H**$_2$=CH), 5.7 (t, —C**H**=CH$_2$).

Siloxane (9): clear, transparent viscous oil, 88% yield, FTIR resonance frequency due to Si—CH$_3$ at 1260 cm^{-1}, —Si—O—Si at 1186 cm^{-1} and 910

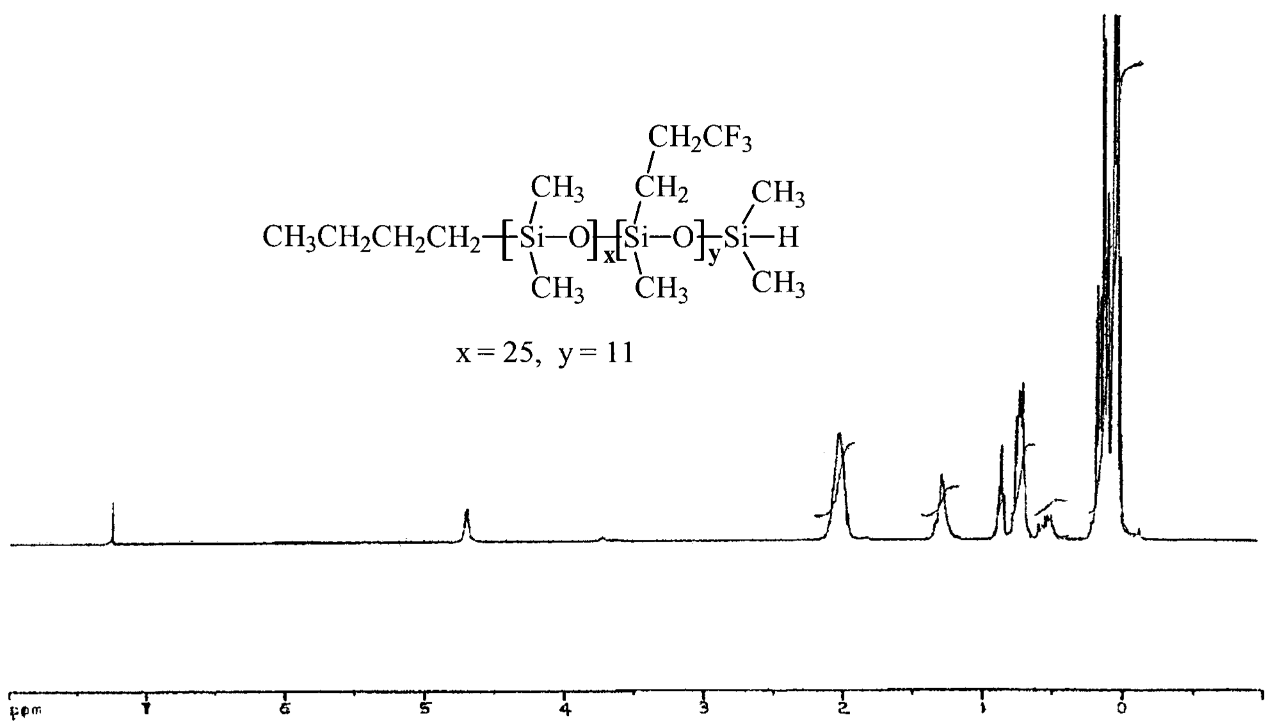

Figure 2 ^{1}H-NMR of silanic hydrogen terminated polyfluorosiloxanes in CDCl$_3$.

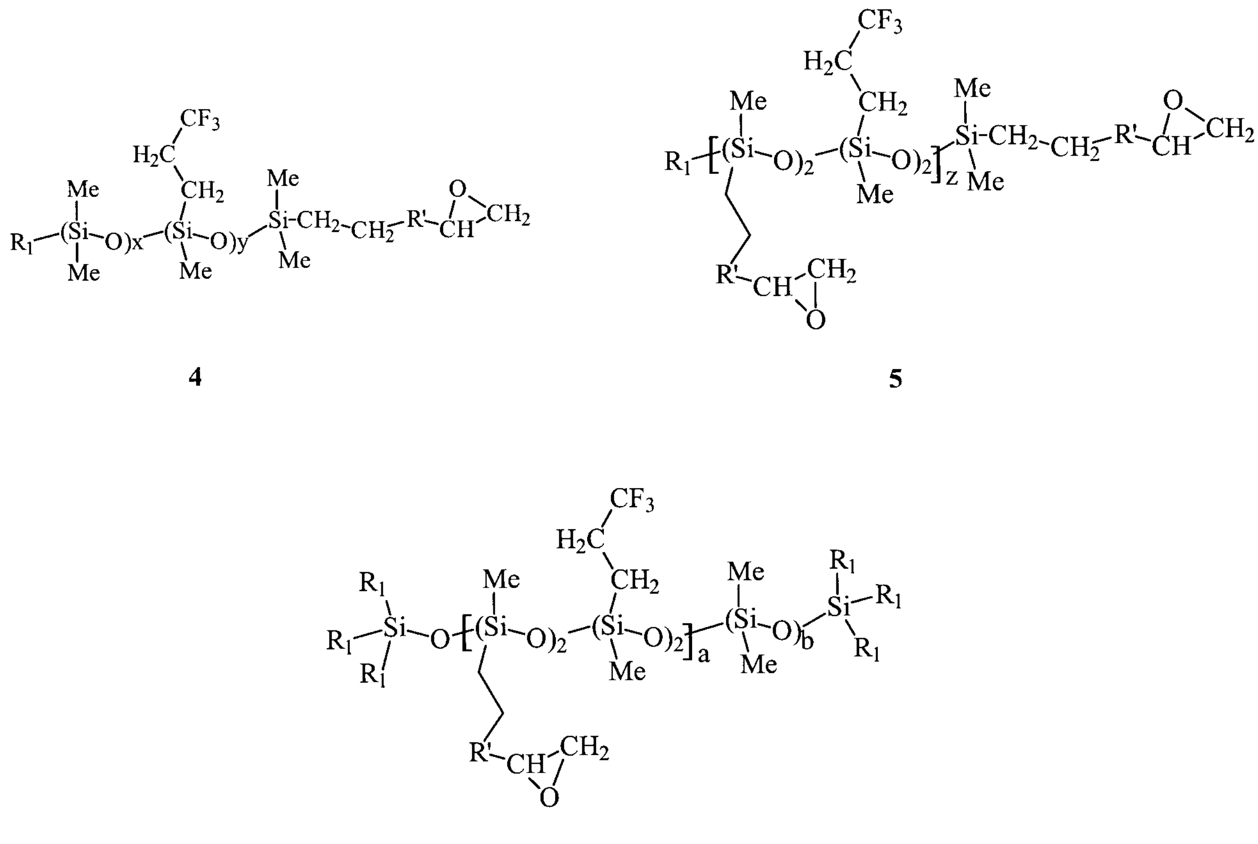

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Figure 3 Epoxy functional polyfluorosiloxanes.

cm^{-1}; ^{1}H-NMR ($CHCl_3$) peaks at δ (ppm) 0.1(s, Si$\mathbf{CH_3}$), 0.5 (t, —$\mathbf{CH_2}$Si), 0.74 (t, $CF_3CH_2\mathbf{CH_2}$—Si—), 1.57 (m, —$\mathbf{CH_2}CH_2$Si—), 2.04 (t, —$\mathbf{CH_2}$—CF3), 2.58 (m, CH(OH)—$\mathbf{CH_2}$—NH, CH_2=CHC$\mathbf{H_2}$NH), 3.85 (m, —, 5.17 (m, $\mathbf{CH_2}$=CH), 5.7 (m, —$\mathbf{CH}$=CH_2).

Synthesis of Quaternary Aminopolyfluorosiloxane

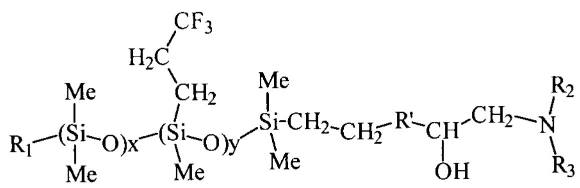
Siloxane (10,11 or 12): si iloxane (7,8 or 9) (2.5 g) in 5 mL toluene was taken in two-necked dry round-bottom flask attached with reflux condenser, and 5 mL of methyliodide was added to it. Reaction mixture was stirred at 60°C for 5 h under the inert atmosphere of nitrogen. After 5 h excess methyliodide and toluene were distilled off. The respective quaternary amino polyfluorosiloxane obtained (10,11, or 12) was then characterized by FTIR, ^{1}H-NMR.

Product Characteristics. Siloxane (10,11): clear, transparent viscous oil, 94% yield, FTIR resonance frequency due to Si—CH_3 at 1260 cm^{-1}, —Si—O—Si— at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR ($CHCl_3$) peaks at δ (ppm) 0.1(s, Si$\mathbf{CH_3}$), 0.5 (t, —$\mathbf{CH_2}$Si), 0.74 (t, $CF_3CH_2\mathbf{CH_2}$—Si—), 0.86 (t, —$\mathbf{CH_3}$), 1.28 (m, —$\mathbf{CH_2}$—), 1.57 (m, —$\mathbf{CH_2}CH_2$Si—), 2.04 (t, —$\mathbf{CH_2}$—CF3), 3.3 (m, Si$(CH_2)_2\mathbf{CH_2}$O$\mathbf{CH_2}$—), 4.5 (m, —N^+—$\mathbf{CH_2}$—C=C—), 5.17 (m, $\mathbf{CH_2}$=CH), 5.7 (m, —$\mathbf{CH}$=CH_2).

Siloxane (12): clear, transparent viscous oil, 92% yield, FTIR resonance frequency due to Si—CH_3 at 1260 cm^{-1}, —Si—O—Si at 1186 cm^{-1} and 910 cm^{-1}; ^{1}H-NMR ($CHCl_3$) peaks at δ (ppm) 0.1(s, Si$\mathbf{CH_3}$), 0.5 (t, —$\mathbf{CH_2}$Si), 0.74 (t, $CF_3CH_2\mathbf{CH_2}$—Si—), 1.57 (m, —$\mathbf{CH_2}CH_2$Si—), 2.04 (t, —$\mathbf{CH_2}$—CF3), 3.3 (m, Si $(CH_2)_2\mathbf{CH_2}$O$\mathbf{CH_2}$—), 4.5 (m, —N^+—$\mathbf{CH_2}$—C=C—), 5.17 (m, $\mathbf{CH_2}$=CH), 5.7 (m, —$\mathbf{CH}$=CH_2).

RESULTS AND DISCUSSION

Silanic hydrogen containing polyfluorosiloxanes undergo hydrosilation with olefinic epoxides in



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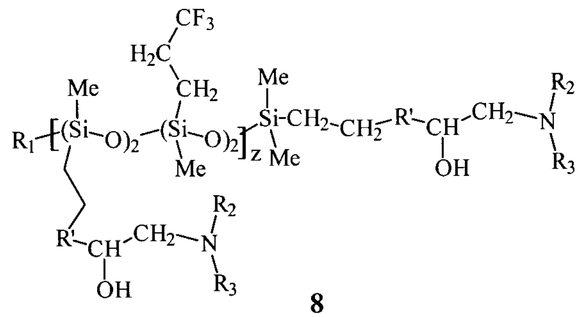

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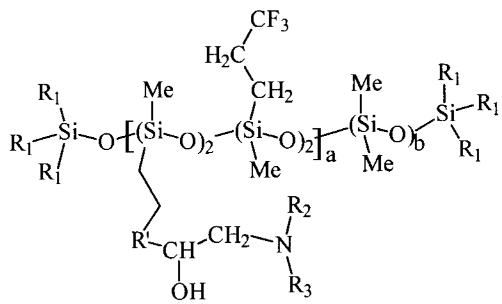

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Figure 4 Amino hydroxy functional polyfluorosiloxanes.

the presence of the platinum–divinyltetramethyldisiloxane complex to give epoxy polyfluorosiloxanes. The commercial fluorosiloxane fluid and elastomers were prepared through ring-opening polymerization of fluorocyclosiloxanes using anionic[12,13] initiators such as butyl lithium[14] or cationic initiators.[15,16] Silanic hydrogen terminated polyfluorosiloxane, (1) was synthesized by ring-opening copolymerization of hexamethylcyclotrisiloxane and 1,3,5-tris(3,3,3-trifluoropropyl), 1,3,5-trimethyl cyclotrisiloxanes using butyllithium at 15°C followed by addition of chlorodimethylsilane. Control in the molecular weight was achieved by varying butyllithium concentration (refer Table I).

Cohydrolysis of dichloromethylsilane and 3,3,3 trifluoropropyl, methyl dichlorosilane was carried out in ether/water system to give a mixture of fluorocyclosiloxane and high molecular weight polymer. After complete removal of HCl, the silanic hydrogen containing fluorocyclosiloxane was distilled at 140°C under vacuum and characterized by FTIR and ^{1}H-NMR. Silanic hydrogen containing polyfluorosiloxanes (2) were obtained by ring-opening polymerization of silanic hydrogen containing fluorocyclosiloxane using butyllithium initiator followed by termination with chlorodimethylsilane at 15°C. The molecular weight was determined using ^{1}H-NMR using integration values of peaks due to Si—H, $SiCH_3$ and butyl protons.

Alternatively, Silanic hydrogen containing polyfluorosiloxane (3) was synthesized by copolymerization of hexamethylcyclotrisiloxane (or octamethylcyclotetrasiloxane), silanic hydrogen containing fluorocyclosiloxane, and hexamethyldisiloxane in the presence of trifluoromethanesulfonic acid.[17] The structures of silanic hydrogen containing siloxanes are indicated in Figure 1, where x = 7–40, y = 3–20, a = b = 5–40, z = 5–30, R_1 = butyl group. Figure 2 indicates the ^{1}H-NMR of silanic hydrogen containing polyfluorosiloxane (1).

Silanic hydrogen containing polyfluorosiloxanes (1,2,3) were further converted to epoxy polyfluorosiloxane by reacting with olefinic epoxide in the presence of the platinum–divinyl tetramethyldisiloxane complex. The olefinic epoxides used was allyl glycidyl ether. The epoxy polyfluorosiloxanes (4,5,6) were further reacted with different amines to give amino hydroxy polyfluorosiloxanes (7,8,9). The general formula of the primary and secondary amines used is R_2R_3NH, where, R_2 is the monovalent hydrocarbon radical and R_3 is the

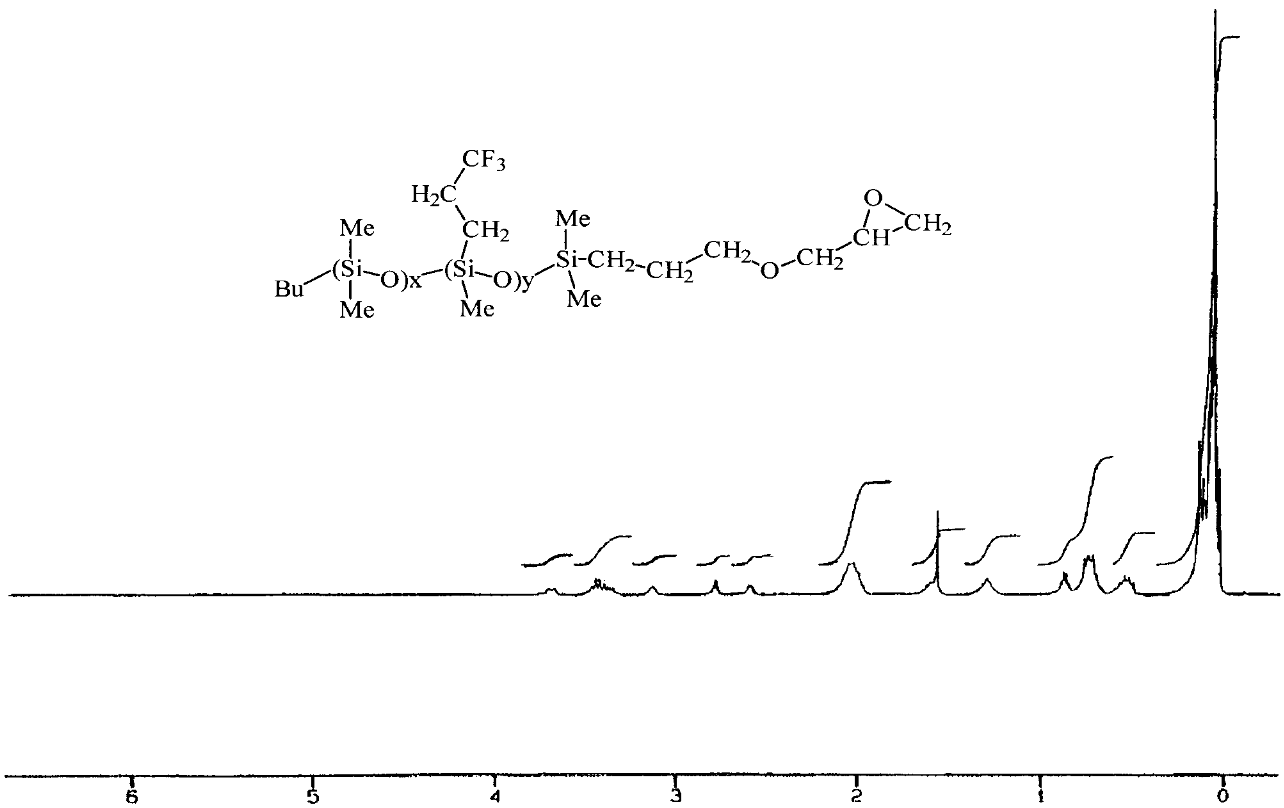


Figure 5 ^{1}H-NMR of epoxy terminated polyfluorosiloxane in $CDCl_3$.

hydrogen or monovalent hydrocarbon radical. The most preferred amine used was allylamine and diethylamine. The general structures of epoxy polyfluorosiloxanes obtained are shown in Figure 3, where, R_1 = monovalent hydrocarbon radical; R' = the divalent hydrocarbon radical, divalent hydrocarbonoxy radical where oxygen is present in the form of ether linkage. X = 7–40, Y = 3–20, Z = 5–30, a,b = 5 = 40.

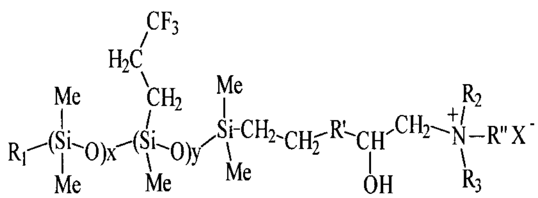
Figure 4 shows the general structures of the amino hydroxy functional polyfluorosiloxanes where, R_1,R_2, = the monovalent hydrocarbon radical; R_3 = H or the monovalent hydrocarbon radical, R' = the divalent hydrocarbon radical, divalent hydrocarbonoxy radical, where oxygen is present in the form of an ether linkage; X = 7–40, Y = 3–20, Z = 5–30, a,b = 5 = 40. Figure 5 shows ^{1}H-NMR of epoxy terminated polyfluorosiloxane obtained by reaction of silanic terminated polyfluorosiloxanes with allyl glycidyl ether.

Amino hydroxypolyfluorosiloxanes were further converted into quaternary amino polyfluorosiloxanes by reaction with alkyl halide. The structures of quaternary aminopolyfluorosiloxanes are shown in Figure 6, where, R_1,R_2,R_3 = the monovalent hydrocarbon radical; R' = the divalent hydrocarbon radical, divalent hydrocarbonoxy radical where oxygen is present in the form of an ether linkage. X = 7–40, Y = 3–20, Z =5–30; R'' = H or the monovalent hydrocarbon radical. Figure 7 indicates the ^{1}H-NMR of the quaternary amino-terminated polyfluorosiloxane.

Surface Activity of Quaternary Amino Polyfluorosiloxanes

The surface-active properties of these quaternary amino polyfluorosiloxanes in water were studied by surface tension measurements (as explained in the Experimental section). Figure 8 shows the plot of surface tension of water vs. the log of concentration of quaternary amino polyfluorosiloxane (in mM).

The minimum surface tension of the quaternary amino siloxane surfactant varied between 21–28 mN/m.[18–20] This was explained to be due to the formation of the siloxane monolayer on the water surface exposing methyl groups to the air. The above-synthesized quaternary amino polyfluorosiloxanes show comparatively high surface



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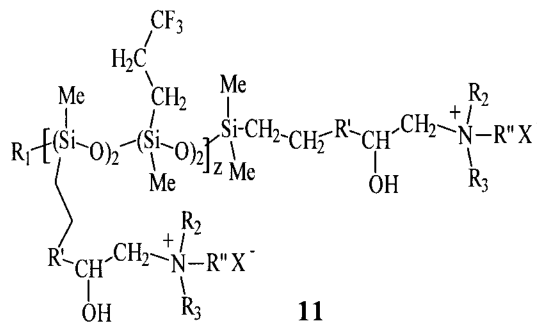

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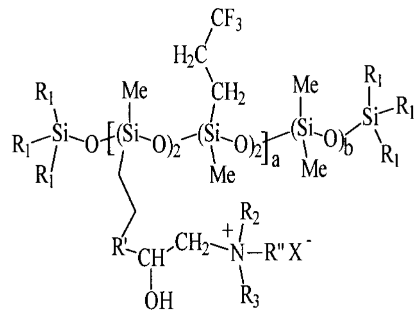

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Figure 6 Quaternary amino polyfluorosiloxanes.

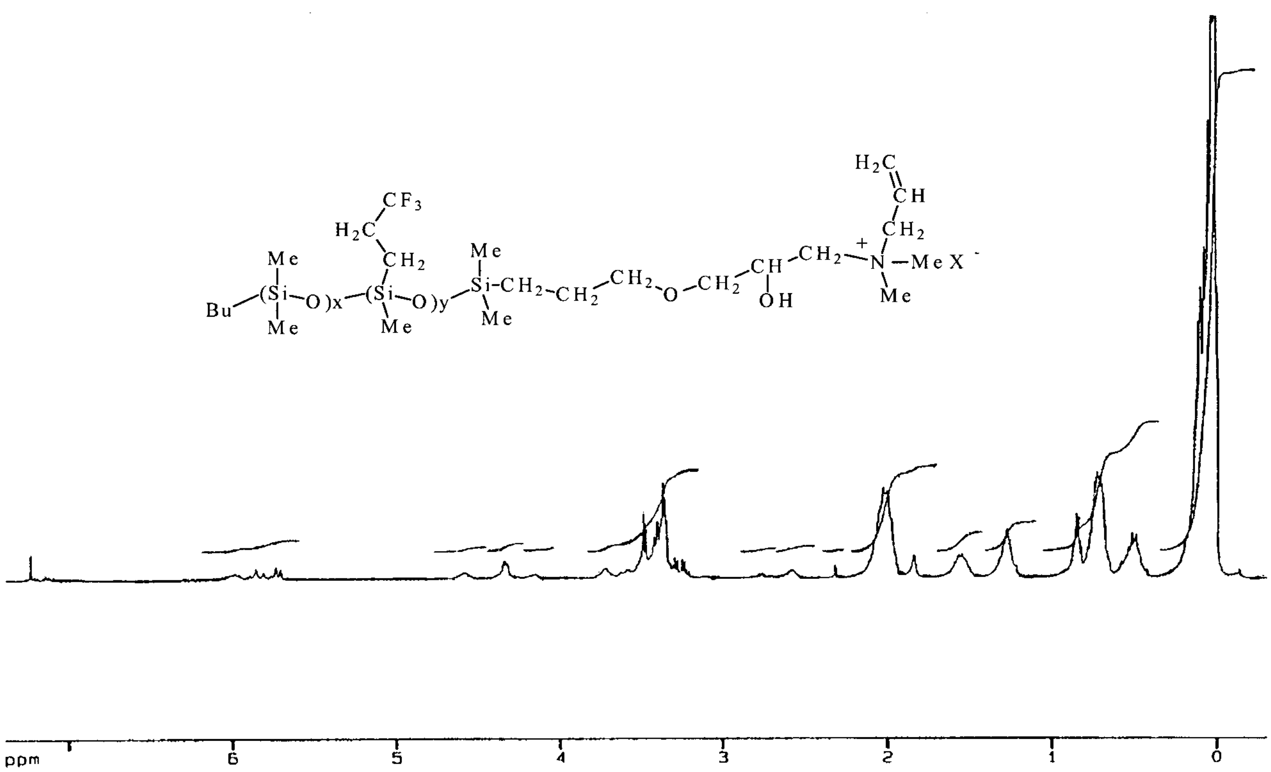

Figure 7 Indicates ^{1}H-NMR of quaternary amino-terminated polyfluorosiloxane.

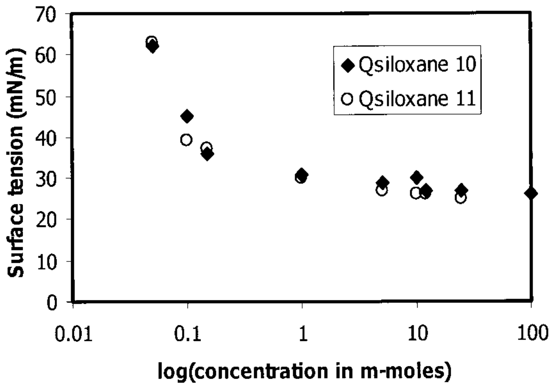

Figure 8 Surface tension of water as a function of the concentration quaternary amino polyfluorosiloxane.

tension (25–26 mN/m). In this case, the siloxane monolayer is formed on the water surface by exposing methyl and 3,3,3 trifluoropropyl group to the air. It is perhaps due to the presence of the —CH_2CH_2— group that does not reach the surface tension quite as low as 21 mN/m, seen with some siloxane surfactants. We ensure that these molecules can be used as good emulsifiers for certain paint or coating applications. To further understand surface behavior of the quaternary amino polyfluorosiloxane surfactant, we are currently investigating the adsorption of quaternary amino polyfluorosiloxane at the air–water interface, aggregation behavior in various solvents of varying dielectric constants, and vesicle formation in aqueous solution.

Antibacterial Activity of Quaternary Amino Fluorosiloxane

Quaternary amino fluorosiloxanes were found to be antibacterial agents. The agar medium and the 0.5% aqueous solution of quaternary amino fluorosiloxanes were autoclaved separately prior to the experiment. Bacillus (2.5 mL) (Gram-negative bacteria) suspension with concentration of cells/mL and 5 mL aqueous solution of quaternary fluorosiloxane were added to 50 mL autoclaved agar broth. A suspension of 2.5 mL bacillus in 50 mL broth was made for the blank experiment. The dilutions were incubated at 37°C for 48 h. No growth was found in the broth containing aqueous solution of quaternary amino fluorosiloxanes.

CONCLUSION

The quaternary amino polyfluorosiloxane obtained from silanic hydrogen containing polyfluorosiloxane. They were found to be excellent surface-active agents.

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