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SYNTHESIS AND STUDIES ON SURFACE ACTIVE WATER SOLUBLE DERIVATIVES OF SILOXANE OLIGOMERS

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Key Words: Quaternary Aminosiloxane, Synthesis, Surface Active, Hydrosilation, Mechanism

ABSTRACT

We report the synthesis of cationic water-soluble siloxanes by reacting aminosiloxanes with dimethyl, n-dodecyl 3-chloro-2-hydroxypropyl quaternary ammonium iodide (DDCQA). Tetramethyl disiloxane on hydrosilation with allyl amine in the presence of hexachloroplatinic acid/IPA gave bis(3-aminopropyl)octamethyltetrasiloxane. In addition, formation of Si-H containing oligomeric siloxanes were detected during this reaction and the extent of formation of the oligomers was found to depend upon the concentration of platinum. The oligomerization reaction was explained by dehydrogenative coupling of Si-H groups in the presence of platinum catalyst. A plausible mechanism for formation of aminosiloxane and the Si-H oligomers were proposed. Alternatively, cyclic Si-H containing siloxanes on polymerization using butyl lithium gave oligomeric Si-H containing siloxanes, which were hydrosilated to give aminosiloxanes. The quaternary aminosiloxanes synthesized showed lowering in surface tension of water to 26 mN/m.

INTRODUCTION

Synthesis and properties of quaternary ammonium derivatives of siloxane oligomers have evoked much research interest in recent time due to their industrial application as surfactants. Synthetic procedures for quaternary aminosiloxanes describe (1) reaction of epoxy [1, 2] or halogenated siloxane [3, 4, 5, 6] with amines followed by quaternization, (2) reaction of carboxylic acid functional quaternary ammonium compounds with amino propyl trialkoxy silane/siloxane [7] compounds and (3) hydrosilation of alkenyl amine in the presence of platinum catalyst followed by quaternization [8, 9]. Among the various approaches described above, hydrosilation has been the most widely used synthetic procedure for aminosiloxane, which were further converted into water-soluble quaternary aminosiloxanes. Addition of Si-H group to allylamine [8], N-N-diethyl allylamine [9] and diallyl methylamine in the presence of hexachloroplatinic acid catalyst at higher temperature was reported to give aminosiloxanes. Hydrosilation of tetramethyldisiloxane (TMDS) with allyl amine in the presence of hexachloroplatinic acid was shown to give cyclic disiloxazane, which was then converted into bis(3-aminopropyl)octamethyltetrasiloxane by hydrolysis at high temperature [10].

We have investigated single step hydrosilation of TMDS with allylamine in the presence of $\text{H}_2\text{PtCl}_6/\text{IPA}$ catalyst and the product was found to be a mixture of aminosiloxane and Si-H oligomer. The formation of oligomer was not reported earlier [8, 9, 10]. We have also investigated the effect of platinum catalyst in directing the reaction, and a plausible mechanism was proposed. Alternatively, Si-H containing oligomer was synthesized by ring opening polymerization of Si-H containing cyclic siloxane using butyl lithium and then the living polymer was terminated with trimethyl chlorosilane. This product was hydrosilated with allylamine. Water-soluble quaternary amino terminated siloxanes were then synthesized by reacting the above mentioned aminosiloxanes with dimethyl, n-dodecyl, 3-chloro-2-hydroxypropyl, quaternary ammonium chloride (DDCQA).

EXPERIMENTAL

Instruments

FT-IR and NMR were carried out using a BOMEN IR spectrophotometer and a Bruker ACP 200 spectrometer (200 MHz), respectively. CDCl_3 and D_2O were used as solvents for the NMR studies. The surface tension measurements were carried out using a Kruss tensiometer K10 at 25°C.

Reagents

The following reagents were used. Dimethylchlorosilane (96%, Fluka); Dimethyldichlorosilane (98%, Spectrochem, India), Dichloromethylsilane (98%, Fluka), Hexachloroplatinic acid (Fisher Scientific Company, New Jersey), Allyl amine (98%, Lancaster), dimethyl, n-dodecyl-3-chloro-2-hydroxypropyl quaternary ammonium chloride (DDCQA), THF (HPLC grade, ex. S. D. Chemicals, India) distilled over sodium, Toluene (HPLC grade ex. S. D. Chemicals, India) dried over sodium.

General Synthetic Procedure

Tetramethyldisiloxane (A1) on hydrosilation with allyl amine in the presence of hexachloroplatinic acid gave bis(3-aminopropyl)octamethyltetrasiloxane (B1) [Figure 1, Scheme 1]. The hydrosilation reaction was studied using $^1\text{H-NMR}$. Aminosiloxane was reacted with dimethyl, n-dodecyl, 3-chloro-2-hydroxypropyl, quaternary ammonium chloride (DDCQA) to give an amber colored water-soluble quaternary amino terminated siloxane (Figure 4, Scheme 2).

Alternatively, heptamethylcyclotetrasiloxane (A2) was synthesized by hydrolyzing a mixture of dimethyldichlorosilane and methylchlorosilane which underwent ring opening polymerization on addition of butyl lithium, resulting in the formation of Si-H containing siloxane. Aminosiloxane was then obtained by hydrosilation of Si-H containing oligomers (B2), on treatment with DDCQA gave water soluble siloxane (D2) (Figure 5, Scheme 3).

Synthesis of Tetramethyldisiloxane (A1)

30 mL of dimethylchlorosilane was added dropwise to 60 mL of water in a 100 mL two-necked flask at 10°C . The mixture was stirred for 2 hours. The aqueous layer was then separated and the organic layer was washed with distilled water till the pH was neutral. Tetramethyldisiloxane then obtained was dried over anhydrous sodium sulfate and characterized by FT-IR and $^1\text{H-NMR}$.

Siloxane (A1): Clear transparent liquid, 81% yield, FT-IR resonance frequency due to Si-H at 2127 cm^{-1} , Si-CH₃ at 1260 cm^{-1} and -Si-O-Si- at $1050\text{-}1100\text{ cm}^{-1}$; $^1\text{H-NMR}$ peaks at δ 0.17 (Si-CH₃) and 4.67 (Si-H).

Synthesis of Bis(3-aminopropyl)octamethyltetrasiloxane (B1)

10 g (0.175M) of allylamine was placed in a 100 ml three-necked RB flask, and 1.5 mL of H₂PtCl₆ solution (3% IPA) was added to it at 50°C under nitrogen

atmosphere. A solution of 10 g (0.074M) of tetramethyldisiloxane in 60 mL dry toluene was added dropwise to allyl amine-platinum complex and the mixture was stirred at 90°C for 15 hours. The reaction was monitored using FT-IR (disappearance of resonance frequency due to Si-H group at 2127 cm⁻¹). On completion of the reaction, platinum catalyst was filtered off and the excess allyl amine and toluene were distilled off under vacuum. The crude product thus obtained was redissolved in 30 mL toluene and 6 mL HBr in acetic acid (35% solution) was added to it at 10°C till pH was acidic. The product (quaternary aminosiloxane) was then extracted twice with water (50 mL) and the product was then reprecipitated from aqueous layer by addition of aqueous NaOH solution and extracted in toluene. Toluene was distilled off and the product was dried under vacuum and characterized by FT-IR and ¹H-NMR spectroscopy.

Siloxane (B1): Pale yellow liquid, 84% yield, FT-IR resonance frequency due to Si-NH₂ at 3358 cm⁻¹ and 3285 cm⁻¹, Si-CH₃ at 1260 cm⁻¹ and -Si-O-Si- at 1050-1100 cm⁻¹; ¹H-NMR peaks at δ 0.06 (Si-CH₃), 0.51 (Si-CH₂), 1.43 (-CH₂) and 2.65 (-CH₂-NH₂).

Synthesis of Quaternary Amino Terminated Siloxane (E1)

1.7 g of DDCQA was dissolved in 50 mL dry toluene in a 100 mL two-necked flask. A solution of 1 g aminosiloxane in 20 mL dry toluene was added dropwise to it. The reaction mixture was refluxed for 7 hours and then stirred for 5 hours at 90°C. The contents were cooled to R.T. The precipitated viscous oily quaternary ammonium salt was separated and dissolved in water. Water was distilled under vacuum and the product was analyzed by FT-IR and ¹H-NMR.

Siloxane (E1): Amber colored viscous oil, 74% yield, FT-IR resonance frequency due to -CH-OH at 3386 cm⁻¹ and -Si-O-Si- at 1050-1100 cm⁻¹; ¹H-NMR peaks at δ 0.1 (Si-CH₃), 0.60 (-Si-CH₂), 0.83 (-CH₃), 1.24 (-C-CH₂-C-), 2.93 (-CH₂-N⁺H₂-CH₂-CH (OH)-), 3.2 (-N⁺-Me₂-CH₂-) and 3.6(-CH (OH)-CH₂-N⁺-).

Synthesis of Si-H Containing Cyclisiloxane (Heptamethyl Cyclotetrasiloxane) (A2)

150 mL of water and 150 mL of ether were placed in a 500 mL three-necked flask and then cooled to 0°C. A mixture of dichlorodimethylsilane and dichloromethylsilane (mole ratio 1: 1) was added dropwise to it by maintaining the temperature at 0-5°C for 1 hour. After completion of the addition, the reaction mixture was stirred for 15 minutes and the organic layer was washed using distilled water till pH was neutral. The organic layer was then dried over anhydrous sodium

sulfate and the ether was evaporated off. Cyclic siloxane was distilled off under 0.1 mm vacuum at 90°C and characterized by FT-IR and ¹H-NMR spectroscopy.

Siloxane (A2): Clear transparent liquid, 64% yield, FT-IR resonance frequency due to Si-H at 2159 cm⁻¹ and Si-CH₃ at 1260 cm⁻¹; ¹H-NMR peaks at δ 0.066 (SiMe₂), 0.089 (SiMeH), 0.13 (SiHCH₃) and 4.68 (Si-H).

Synthesis of Linear Si-H Siloxane (B2)

12.8 mM butyl lithium was placed into 100 mL dry RB flask containing 50 mL dry THF under nitrogen. A solution of 15 g heptamethylcyclotetrasiloxane (A2) in 20 mL of dry THF was added dropwise at -30°C and the reaction mixture was stirred for 8 hours at 0°C. 2.5 mL trimethylchlorosilane was subsequently added. The reaction mixture was stirred for another 3 hours. The solvent and excess SiMe₃Cl were distilled off under vacuum after separation of LiCl precipitate by filtration. The product was then dried under vacuum and characterized using FT-IR and ¹H-NMR.

Siloxane (B2): Clear transparent oil, 82% yield, FT-IR resonance frequency due to Si-H at 2159 cm⁻¹ and Si-CH₃ at 1260 cm⁻¹; ¹H-NMR peaks at δ 0.089 (SiMe₂), 0.171 (SiHMe), 0.51 (-CH₂-Si), 0.83 (CH₃-C-), 1.66 (-CH₂-) and 4.68 (Si-H).

Synthesis of Aminosiloxane (C2)

Allylamine (0.6M) was placed in a three-necked RB flask and 1 mL of H₂PtCl₆/IPA solution (3%) was added. The Si-H containing siloxane oligomer (B2, 0.1M) in 30 mL toluene was added to the allylamine/Pt complex and the reaction mixture was refluxed till disappearance of Si-H resonance frequency in FT-IR. On completion of the reaction, unreacted allylamine was distilled off after separation of H₂PtCl₆ by filtration. The product was dried under vacuum and characterized by FT-IR and ¹H-NMR.

Siloxane (C2): Light yellow oil, 70% yield, FT-IR resonance frequency due to -NH₂ at 3283 cm⁻¹ and 3363 cm⁻¹, Si-CH₃ at 1260 cm⁻¹ and -Si-O-Si- at 1050-1100 cm⁻¹; ¹H-NMR peaks at δ 0.079 (SiMe₂), 0.094 (SiMeCH₂-), 0.51 (-CH₂-Si), 0.83 (CH₃-C-), 1.66 (-CH₂-) and 2.64 (-CH₂-NH₂).

Synthesis of Quaternary Amino Siloxane (D2)

6 gm aminosiloxane (C2) in 25 mL toluene was added to 4 g DDCQA in 20 mL toluene and placed in a two-necked RB flask. The mixture was stirred for 5

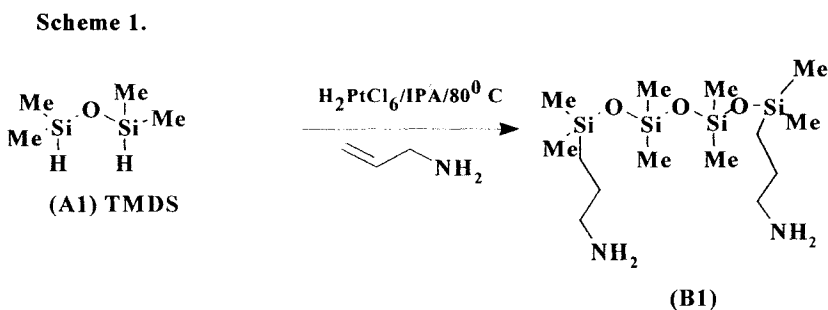


Figure 1. Reaction scheme for synthesis of bis(3-aminopropyl)octamethyltetrasiloxane from TMDS.

hours at 80°C and the oily viscous product formed was separated. The water-soluble product was characterized by FT-IR and $^1\text{H-NMR}$.

Siloxane (D2): Viscous amber colored oil, 82% yield, FT-IR resonance frequency due to $-\text{CH-OH}$ at 3386 cm^{-1} and $-\text{Si-O-Si-}$ at $1050\text{--}1100\text{ cm}^{-1}$; $^1\text{H-NMR}$ peaks at δ 0.1 ($-\text{Si-CH}_3$), 0.60 ($-\text{Si-CH}_2$), 0.83 ($-\text{CH}_3$), 1.24 ($-\text{C-CH}_2\text{-C-}$), 2.93 ($-\text{CH}_2\text{-N}^+\text{H}_2\text{-CH}_2\text{-CH(OH)-}$), 3.2 ($-\text{N}^+(\text{Me})_2\text{-CH}_2-$) and 3.6 ($-\text{CH(OH)-CH}_2\text{-N}^+$).

RESULTS AND DISCUSSION

Synthesis of Amino Siloxane from Tetramethyldisiloxane

Reaction of allylamine with tetramethyldisiloxane, $(\text{HSiMe}_2)_2\text{O}$ in the presence of platinum-1,3 divinyltetramethyl complex was reported to give bis(3-amino-propyl)tetramethyldisiloxane, at room temperature [11]. However, when hexachloroplatinic acid [10] was used as catalyst, cyclic disiloxazane was formed, which then was converted to bis(3-aminopropyl)octamethyltetrasiloxane by hydrolysis at high temperature.

Hydrosilylation of tetramethyldisiloxane (A1) with allylamine in the presence of hexachloroplatinic acid in IPA was now studied in detail. The reaction conditions are described in the Experimental section. The crude product of hydrosilylation was analyzed by $^1\text{H-NMR}$ and FT-IR, and was found to be a mixture of aminosiloxane (B1) (Figure 1, Scheme 1) and Si-H containing siloxane oligomer (C1). The product mixture was separated by extracting the aminosiloxane in water by forming a salt ($\text{HBr/H}_3\text{CCOOH}$) and reprecipitation by aq. NaOH. The pure aminosiloxane

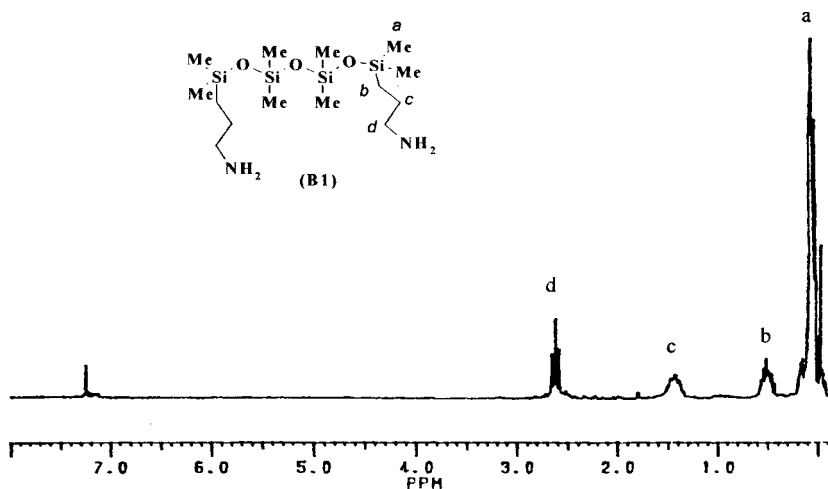


Figure 2a

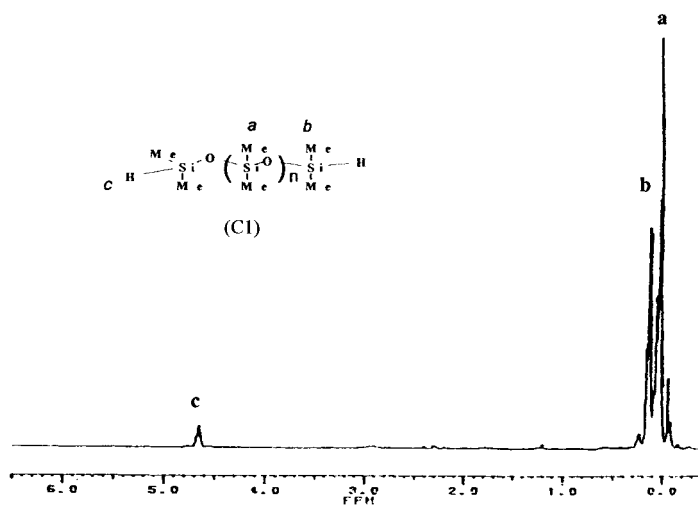


Figure 2b

Figure 2. a) Bis(3-aminopropyl)octamethyltetrasiloxane (B1); b) Si-H oligomer product (C1).

obtained was then characterized by $^1\text{H-NMR}$. ($^1\text{H-NMR}$ peaks due to CH_3SiCH_2 -, $-\text{CH}_2\text{Si}$ -, $-\text{CH}_2$ - $-\text{CH}_2\text{NH}_2$ groups at δ 0.06, 0.5, 1.3, 2.65 ppm, respectively, Figure 2a). The Si-H siloxane oligomer recovered as organic layer was characterized by $^1\text{H-NMR}$ ($^1\text{H-NMR}$ peaks due to Si-CH_3 and Si-H groups at δ 0.07 and 4.65

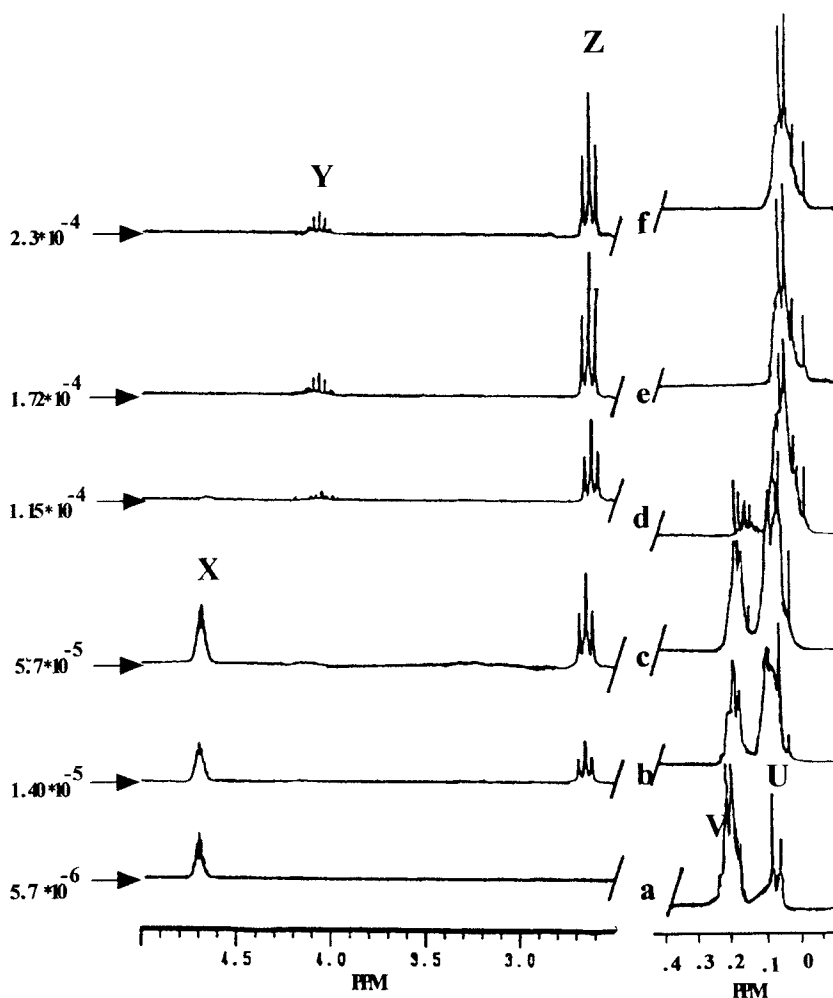
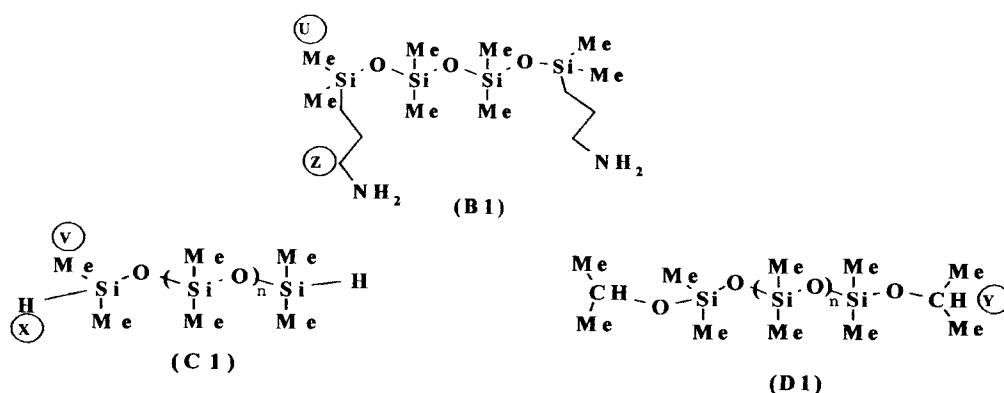


Figure 3. $^1\text{H-NMR}$ of hydrosilation product at different concentration of hexachloroplatinic acid (TMDS, 0.074 moles; Allylamine 0.175 moles).

Figure 2b). The structure of oligomer was assigned to be $\text{H-SiMe}_2\text{O}(\text{SiMe}_2\text{O})_n\text{-SiMe}_2\text{-H}$ where $n = 10$.

The reaction was then carried out under varying platinum concentrations (5.7×10^{-6} M to 2.3×10^{-4} M). The $^1\text{H-NMR}$ of the products at different platinum concentrations is shown in Figure 3. It was observed that at extremely low platinum concentration (5.7×10^{-6} moles) formation of Si-H containing siloxane oligomer was favored. At concentrations of 1.15×10^{-4} moles and above, conversion to

aminosiloxane (B1) was preferred. However, at high platinum concentration, IPA was observed to react with the Si-H groups resulting in the product containing alkoxy siloxane having structure $\text{Me}_2\text{CHOSiMe}_2\text{O}-(\text{SiMe}_2\text{O})_n\text{SiMe}_2\text{OCHMe}_2$ (D1). It was reported earlier that a reaction of Si-H group with alcohol gave alkoxy siloxanes at high temperature [12, 13]. The three products B1, C1, D1, thus obtained are shown below (U, V, X, Y, Z indicates specific peaks of $^1\text{H-NMR}$ spectra in Figure 3).



Synthesis of Oligomeric Aminosiloxane from Cyclic Siloxane

Hydrolysis of a mixture of dichlorodimethylsilane and dichloromethylsilane gave cyclic siloxane (A2) containing Si-H group. This reaction was carried out at different mole proportions of these reactants and it was found that when the ratio was 1:1, heptamethylcyclotetrasiloxane (A2) was formed which was characterized by $^1\text{H-NMR}$ (peak due Si-H at δ 4.65 ppm). Thus, on ring opening, polymerization using butyl lithium gave a living polymer/oligomer which was terminated using trimethylchlorosilane. Hydrosilation of this oligomeric siloxane (B2) with allylamine in the presence of hexachloroplatinic acid gave aminosiloxane (C2) [Figure 5, Scheme 3].

Synthesis of Water-Soluble Siloxane (E1, D2): Reaction of Aminosiloxane with Dimethyl, Dodecyl 3-Chloro-2-Hydroxypropyl Quaternary Ammonium Chloride (DDCQA)

In order to achieve water-soluble siloxane, the aminosiloxanes mentioned above were reacted with dimethyl, dodecyl, 3-chloro-2-hydroxypropyl, quaternary ammonium chloride (DDCQA) [Figures 4, 5]. Here, the amino functionality of the siloxane was reacted with 3-chloro-2-hydroxy group of quaternary salt. The product was characterized by $^1\text{H-NMR}$ in D_2O (Figure 6).

Scheme 2.

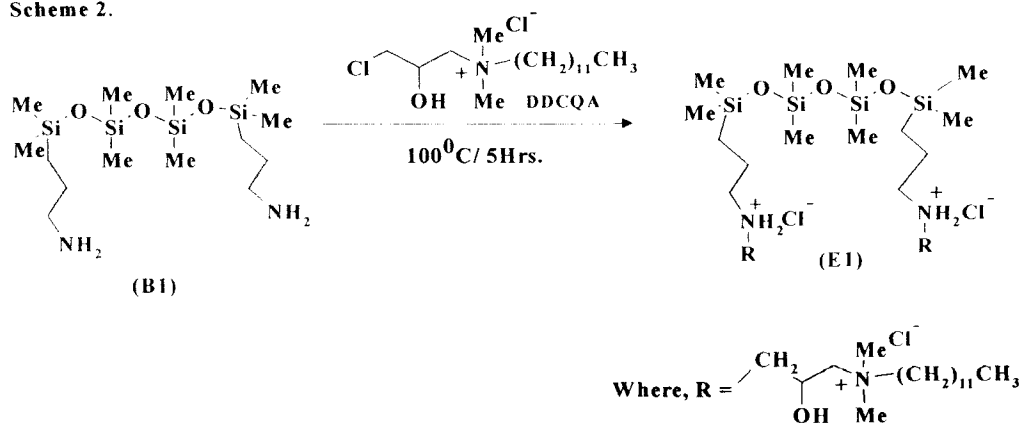


Figure 4. Reaction scheme for synthesis of water soluble siloxane (E1).

Scheme 3.

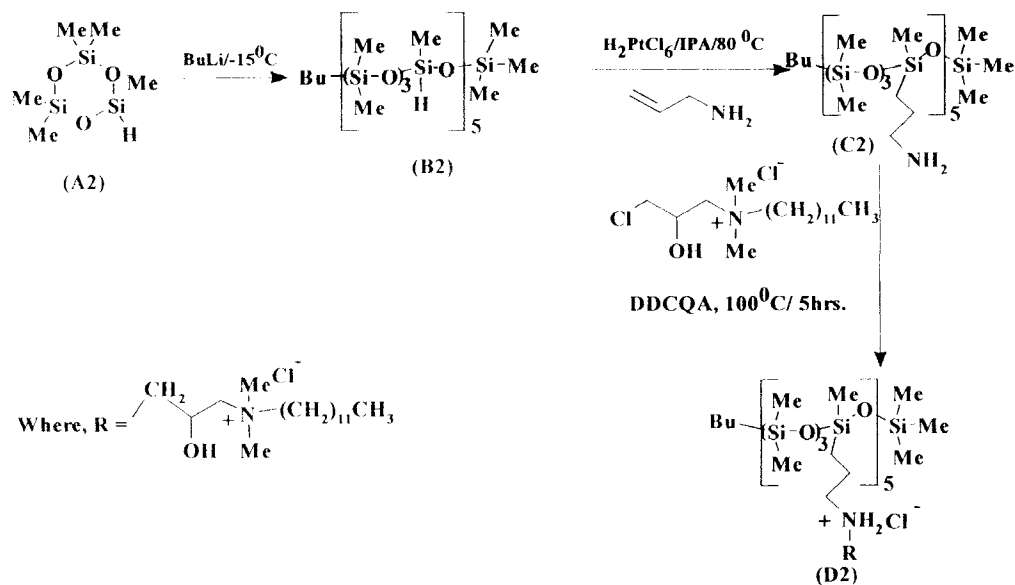


Figure 5. Reaction scheme for synthesis of water soluble siloxane (D2).

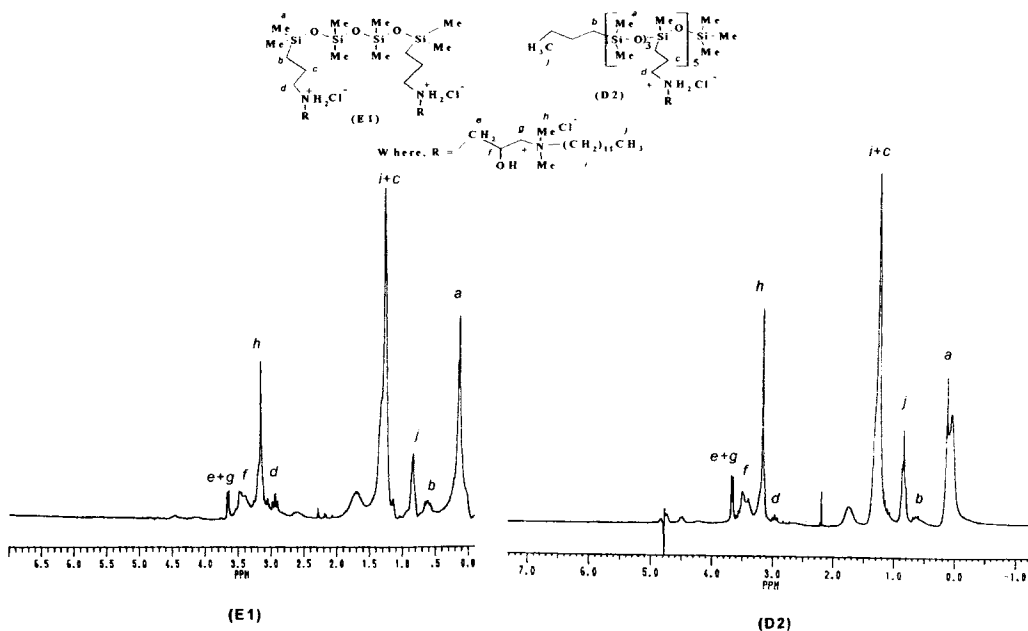


Figure 6. ¹H-NMR of quaternary aminosiloxane (E1), (D2).

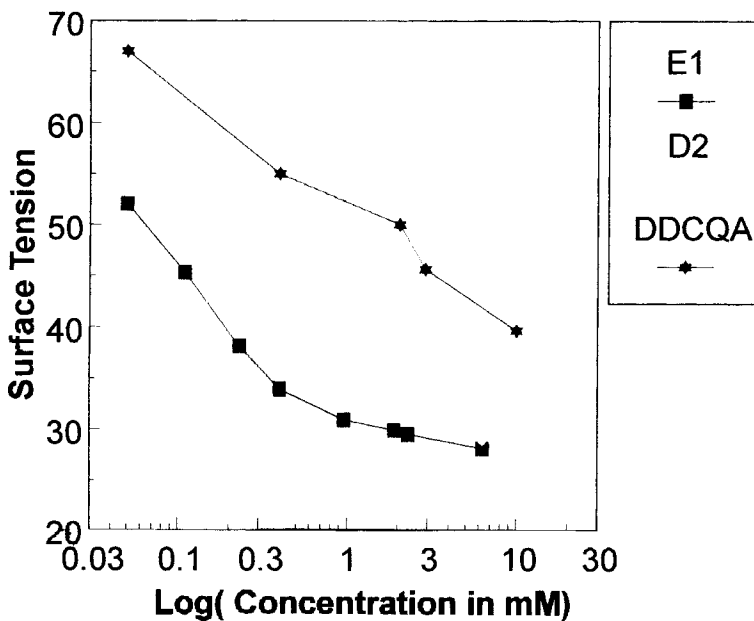


Figure 7. Graph of surface tension of quaternary aminosiloxane (E1 and D2) and DDCQA Vs log (concentration in moles).

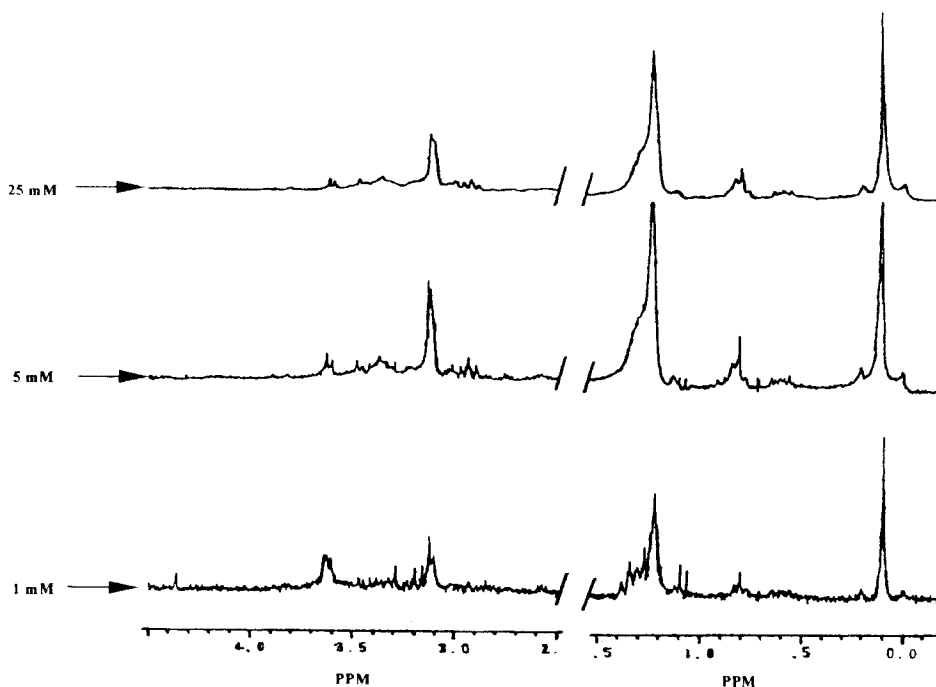


Figure 8. $^1\text{H-NMR}$ spectra of quaternary aminosiloxane at various concentrations.

The product gave a clear solution in water and good lather, and it also lowered surface tension of water to approximately 27. Surface tension was measured at different concentrations as shown in Figure 7.

Aggregation Behavior of Quaternary Aminosiloxane in Water

The aggregation of quaternary aminosiloxane (E1) was studied in D_2O at various concentrations above and below CMC using $^1\text{H-NMR}$. It was found that there was no change in chemical shifts of any protons. There is a difference in the splitting pattern of spectra obtained at concentrations above and below CMC. At concentrations below CMC, the peaks due to SiMe_2 and $-(\text{CH}_2)_n-$ were sharp which broaden at concentration above CMC. Also, there was splitting of peaks due to $-\text{N}^+(\text{CH}_3)_2\text{CH}_2-$. Figure 8 shows the $^1\text{H-NMR}$ spectra of quaternary aminosiloxane (E1) at different concentrations below and above CMC.

As mentioned above, hydrosilation of allylamine with tetramethyldisiloxane in the presence of hexachloroplatinic acid in isopropyl alcohol, gave bis(3-amino-

Scheme 4.

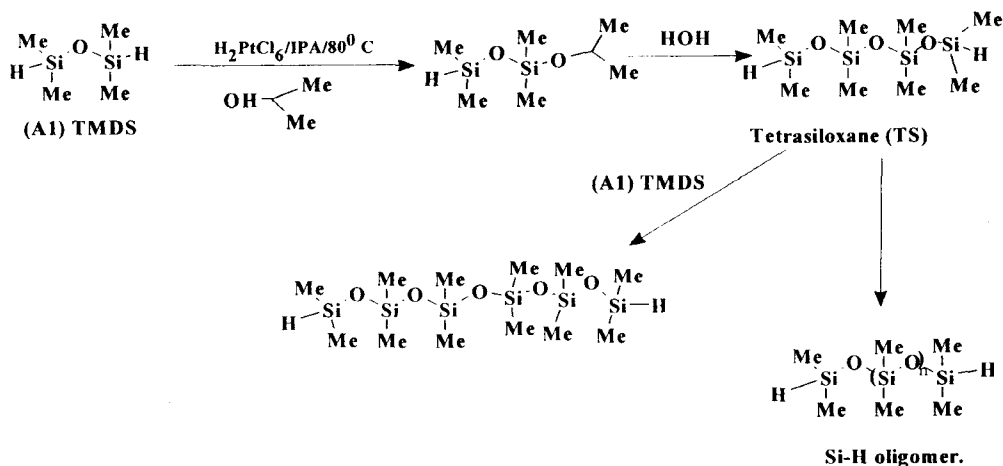


Figure 9. Interference of alcohol in the reaction to give oligomeric siloxane.

propyl)octamethyltetrasiloxane as a dimeric product at higher temperature. There was formation of Si-H containing oligomers, which was not reported earlier during hydrosilation [8, 9, 10]. Formation of oligomeric Si-H containing siloxane was explained as follows.

Boileae *et al.* [12] explained, pentamethyldisiloxane gave silanol in the presence of water (or alcohol) and platinum catalyst, which on reaction with another molecule of pentamethyldisiloxane, gave decamethyltetrasiloxane. Lewis reported formation of colloidal platinum as the intermediate catalytic species [13]. Formation of platinum colloid/ R_3SiH intermediate [14] followed by nucleophilic addition of water or alcohol was reported to give $\text{R}_3\text{Si-OH}$, which reacted, with another R_3SiH to give $\text{R}_3\text{Si-O-SiR}_3$. Also, the presence of transition metals was reported to catalyze dehydrogenative coupling of Si-H silanes to give Si-Si bond formation which on oxidation gave disiloxanes (Si-O-Si) [15].

Based on the above reported results, a mechanism for the formation of Si-H oligomeric siloxanes during hydrosilation can be proposed as follows (Figure 9 Scheme 4). Thus, tetramethyltetrasiloxane undergoes dehydrogenative coupling to give octamethyltetrasiloxane (TS) which further gave Si-H containing siloxane oligomers.

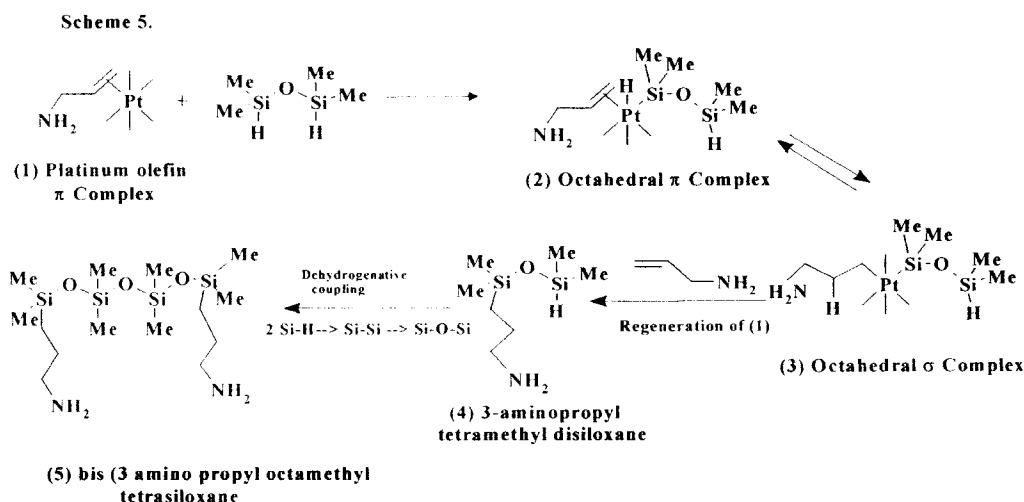


Figure 10. Mechanism of formation of bis(3-aminopropyl)octamethyl tetrasiloxane.

Mechanism

As reported, hydrosilation of allylamine with TMDS using $\text{H}_2\text{PtCl}_6/\text{IPA}$ should lead to bis(3-aminopropyl)tetramethyldisiloxane [11]. However, the main product obtained in this case was bis(3-aminopropyl)octamethyltetrasiloxane. The mechanism of a hydrosilation using chloroplatinic acid had been explained earlier to be by virtue of its reduction to platinum metal [16]. Subsequently, it had been suggested that the reaction takes place under homogeneous conditions [17]. Therefore, the mechanism based on π complexation with olefin and subsequent π - σ rearrangement had been proposed. On this basis, the following mechanistic route for the formation of bis(3-aminopropyl)octamethyltetrasiloxane was proposed (Figure 10).

In the presence of platinum catalyst, activation of olefin takes place by weakening of C=C bond due to coordination with platinum and simultaneous cleavage of Si-H bond resulting into octahedral π complex (2) (Scheme 5). This π complex further undergoes rearrangement to σ complex (3) resulting in formation of 3-aminopropyltetramethyldisiloxane (4). Bis(3-aminopropyl)octamethyltetrasiloxane (B1) was then obtained through dimerization of 3-aminopropyltetramethyldisiloxane (5).

CONCLUSIONS

Hydrosilation of tetramethyldisiloxane with allylamine in the presence of hexachloroplatinic acid in IPA gave bis(3-aminopropyl)octamethyltetrasiloxane. In addition, formation of the Si-H oligomeric siloxane was found to be observed at a low platinum concentration. A plausible mechanism for oligomerization, due to dehydrogenative coupling of Si-H group, was proposed and this was shown to be in agreement with the mechanism explained by Boileau and Lewis. Alternatively, Si-H containing siloxane oligomer obtained by ring opening polymerization of cyclic Si-H siloxane, on hydrosilation with allylamine was also shown to give aminosiloxane. The above aminosiloxanes were converted to quaternary aminosiloxane by reaction with dimethyl, dodecyl chlorohydroxypropyl quaternary ammonium chloride (DDCQA). The water soluble product obtained was thus shown to have excellent surface-active properties.

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