Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

SYNTHESIS AND STUDIES ON STARCH-G-QUATERNARY AMINO POLYSILOXANE GRAFT COPOLYMERS

Ashish Vaidya[a]; V. G. Kumar
[a] Chemical Engineering Department, Iacocca Hall, Lehigh University, Bethlehem, PA, U.S.A.

To cite this Article Vaidya, Ashish and Kumar, V. G.(1999) 'SYNTHESIS AND STUDIES ON STARCH-G-QUATERNARY AMINO POLYSILOXANE GRAFT COPOLYMERS', Journal of Macromolecular Science, Part A, 36: 9, 1323 — 1336
To link to this Article: DOI: 10.1081/MA-100101600
URL: http://dx.doi.org/10.1081/MA-100101600

J.M.S.—PURE APPL. CHEM., A36(9), pp. 1323–1336 (1999)

SYNTHESIS AND STUDIES ON STARCH-G-QUATERNARY AMINO POLYSILOXANE GRAFT COPOLYMERS

Ashish Vaidya*

Chemical Engineering Department
Iacocca Hall
Lehigh University
Bethlehem, PA 18015

V. G. Kumar

Hindustan Lever Research Center
Mumbai 400 099, India

ABSTRACT

The functional quaternary amino polydimethylsiloxane, e.g. 3-chloro-2-hydroxypropyl, methyl, n-propyl, quaternary amino polydimethylsiloxane was prepared and reacted with starch to obtain water soluble starch-g-quaternary amino polydimethylsiloxane (SQPDMS) copolymer. Monofunctional epoxy terminated polydimethylsiloxane (PDMS) was reacted with n-propylamine to give n-propyl aminohydroxy polydimethylsiloxane which on further reaction with epichlorohydrin followed by quaternization using methyliodide gave 3-chloro-2-hydroxypropyl, methyl, n-propyl quaternary amino polydimethylsiloxane (QPDMS). SQPDMS copolymer has higher surface activity than quaternary amino PDMS and cationic starch derivatives containing hydrocarbon moieties.

---

* Author to whom correspondence should be addressed.

www.dekker.com

INTRODUCTION

Synthesis of amphiphilic polymers, consisting of polydimethylsiloxane as the hydrophobic and carbohydrate as the hydrophilic moiety, has been receiving considerable attention in the recent years, due to their interesting properties and widespread industrial applications. Polydimethylsiloxane (PDMS) network containing sucrose as the crosslinking unit exhibits excellent biocompatibility, good mechanical and optical properties [1]. These amphiphilic polymers are generally divided into two categories. The first category consists of small carbohydrate moieties covalently linked to the PDMS backbone. These are synthesized by hydrosilation of allyl functionalized carbohydrate derivatives with silanic hydrogen containing PDMS, in the presence of platinum catalyst [2, 3] or by reaction of unprotected aldonolactone with amino functionalized PDMS [4, 5]. In the second category, the PDMS chains are grafted to polysaccharide backbone. These are obtained by the reaction of polysaccharide (e.g. starch) backbone with modified PDMS [6, 7]. The starch obtained in this case is hydrophobic in nature. Water soluble starches grafted with PDMS have not yet been reported. But there are few reports on water soluble cationic starches containing hydrocarbon units [8, 9]. These are prepared by reaction of 3-chloro-2-hydroxypropyl, trialkyl quaternary ammonium chlorides with starch in basic medium.

Our objective is to incorporate both PDMS and quaternary amino moieties in starch to obtain water soluble starch with better surface-active properties than that of cationic starch containing hydrocarbon units. In this paper, we report synthesis of surface-active starch-g-quaternary amino PDMS (SQPDMS) copolymer by reacting 3-chloro-2-hydroxypropyl, methyl, n-propyl quaternary amino PDMS (QPDMS) with granular as well as degraded starches (lower molecular weight). The SQPDMS copolymer obtained was found to be more surface-active than cationic starch containing hydrocarbon units. The surface-activity was regulated by changing the number of siloxane units in the graft copolymer.

EXPERIMENTAL

Methods

FTIR analysis was carried out using BOMEN FTIR spectrophotometer. ^{1}H-NMR spectra were recorded on Bruker ACP 200 MHz using $CDCl_3$ and D_2O

as the solvent. Chemical shifts of various peaks in the spectra were referenced with respect to the HDO peak appearing at (δ 4.78 in D_2O and the $CHCl_3$ peak appearing at (δ 7.26 in $CDCl_3$. The surface tension measurements were carried out using Kruss tensiometer K10, at 25°C.

Chemicals

Hexamethylcyclotrisiloxane (98%, Aldrich); butyllithium (1.6 M solution in hexane, Fluka); chlorodimethylsilane (96%, Fluka); allyl glycidyl ether (97%, Lancaster); hexachloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$ (3% solution of hexachloroplatinic acid in isopropyl alcohol, (IPA) was used for hydrosilation reaction, Fisher Scientific Company, New Jersey); n-propylamine (98%, Lancaster); epichlorohydrin (98%, SISCO Research Laboratory); methyliodide (99%, SISCO Research Laboratory); THF (refluxed over sodium using benzophenone indicator); toluene (dried over sodium).

Overall Reaction Scheme

Monoepoxy terminated PDMS were obtained by hydrosilation of monofunctional silanic hydrogen terminated linear PDMS with allyl glycidyl ether in the presence of hexachloroplatinic acid. The epoxy group was opened up using n-propylamine to give n-propyl aminohydroxy PDMS. This was on further reaction with epichlorohydrin followed by quaternization using methyliodide gave 3-chloro-2-hydroxypropyl, methyl, n-propyl, quaternary amino PDMS (QPDMS). The QPDMS was reacted with starch in the presence of basic medium to give starch-g-quaternary amino PDMS copolymer (SQPDMS).

Synthesis of Monofunctional Silanic Hydrogen Terminated PDMS (1)

0.02 moles of n-butyllithium (n-BuLi) in n-hexane was placed in a three-necked dry flask containing 60 mL of dry THF at –15°C under the inert atmosphere of nitrogen. A solution of 25 g hexamethyl cyclotrisiloxane (D_3) in 40 mL dry THF was injected into the flask containing n-BuLi/THF solution and the reaction mixture was stirred at –15°C for 20 hours under the nitrogen atmosphere. The living polymer was then terminated by an addition of 4 mL of chlorodimethyl silane (HMe_2SiCl). Excess chlorodimethylsilane and solvent were distilled off under vacuum at 35°C and the LiCl precipitate was filtered off. The product was washed with water to remove last traces of LiCl percipitate. The monofunctional silanic hydrogen terminated PDMS was then characterized using FTIR and ^{1}H-NMR.

Product Characteristics

Clear, transparent liquid, 89% yield, FTIR peak due to Si-H at 2159 cm^{-1}, Si-CH_3 at 1260 cm^{-1}, -Si-O-Si- at 1186 cm^{-1}; ^{1}H-NMR ($CDCl^3$, ppm) peaks at (δ 0.089 (s, Si(C$\underline{\mathbf{H}}_3$)$_2$), 0.171(s, SiHC$\underline{\mathbf{H}}_3$), 0.5 (t, -C$\underline{\mathbf{H}}_2$Si), 0.86 (t, -C$\underline{\mathbf{H}}_3$), 1.57 (m, -C$\underline{\mathbf{H}}_2$-C$\underline{\mathbf{H}}_2$-CH_3) and 4.68 (s, Si-$\underline{\mathbf{H}}$).

Synthesis of Epoxy Terminated PDMS (2)

9.2 g (0.08 moles) of allyl glycidyl ether (AGE) was placed in a two-necked dry round bottom flask and 0.5 mL of 3% solution of hexachloroplatinic acid in isopropyl alcohol (IPA) was added, and the mixture was stirred at 0°C for ten minutes under the nitrogen atmosphere. A solution of 25 g (0.02 moles) of silanic hydrogen terminated PDMS (1) in a 75 mL dry toluene was added drop-wise to the allyl glycidyl ether-platinum complex and the reaction mixture was stirred at 25°C till the disappearance of the peak at 2159 cm^{-1} due to Si-H in FTIR. Toluene and excess AGE were distilled off under vacuum. The epoxy PDMS obtained was characterized by FTIR and ^{1}H-NMR.

Product Characteristics

Clear, transparent oil, 95% yield, FTIR peaks due to, Si-CH_3 at 1260 cm^{-1}, -Si-O-Si- at 1186 cm^{-1}; ^{1}H-NMR ($CDCl^3$, ppm) peaks at (δ 0.1(s, SiC$\underline{\mathbf{H}}_3$), 0.5 (t, C$\underline{\mathbf{H}}_2$Si), 0.86 (t, -C$\underline{\mathbf{H}}_3$), 1.32 (m, -C$\underline{\mathbf{H}}_2$$CH_2$Si-), 1.57 (m, -C$\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2$$CH_3$), 2.7(d, epoxy -C$\underline{\mathbf{H}}_2$), 3.13 (m, epoxy -C$\underline{\mathbf{H}}$), 3.4 (m, -C$\underline{\mathbf{H}}_2OC\underline{\mathbf{H}}_2$$(CH_2)_2$Si).

Synthesis of n-Propyl Aminohydroxy PDMS (3)

A solution of 13.6 g (0.01 moles) of epoxy PDMS (2) in 25 mL toluene was placed in a three-necked dry round bottom flask attached with a reflux condenser. 6 g (0.1 moles) of n-propylamine was added and the reaction mixture was refluxed at 100°C for 7 hours with cold water circulation, under the dry nitrogen atmosphere. Excess n-propylamine and toluene were distilled off and the product obtained was characterized by FTIR, ^{1}H-NMR.

Product Characteristics

Clear, pale yellow, viscous oil, 97% yield, FTIR peaks due to CH-OH at 3407 cm^{-1}, Si-CH_3 at 1260 cm^{-1}, -Si-O-Si- at 1186 cm^{-1}; ^{1}H-NMR ($CDCl_3$, ppm) peaks at (δ 0.1(s, SiC$\underline{\mathbf{H}}_3$), 0.5 (t, -C$\underline{\mathbf{H}}_2$Si), 0.86 (t, -C$\underline{\mathbf{H}}_3$), 1.32 (m, -C$\underline{\mathbf{H}}_2$$CH_2$Si-), 1.55 (m -C$\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2$$CH_3$), 2.5 (t, -NHC$\underline{\mathbf{H}}_2$$CH_2CH_3$), 2.58 (d, CH(OH)-C$\underline{\mathbf{H}}_2$-NH), 3.4 (m, -C$\underline{\mathbf{H}}_2OC\underline{\mathbf{H}}_2$$(CH_2)_2$Si) and 3.85 (m, -C$\underline{\mathbf{H}}$(OH)).

Synthesis of 3-Chloro-2-hydroxypropyl, Methyl, n-Propyl Quaternary Amino Terminated PDMS (QPDMS) (5)

A solution of 14.2 g (0.01 moles) of (3) in 25 mL toluene wasplaced in a two-necked dry round bottom flask and 9.2 g (0.1 moles) of epichlorohydrin was added to it. Reaction mixture was stirred at 80°C for 8 hours under the nitrogen atmosphere. Excess epichlorohydrin and solvent were distilled off. The 3-chloro-2-hydroxypropyl, n-propyl, aminohydroxy PDMS (4) obtained was characterized by FTIR and ^{1}H-NMR. Excess methyliodide was added to (4) and reaction mixture was refluxed under cold water circulation at 60°C for 6 hours. Unreacted methyliodide was distilled off and QPDMS (5) was isolated and characterized by FT-IR, ^{1}H -NMR.

Product Characteristics

3-Chloro-2-hydroxypropyl, n-propyl aminohydroxy PDMS (4): clear, pale yellow oil, 95% yield, FT-IR peaks due to CH-OH at 3407 cm^{-1}, $Si\text{-}CH_3$ at 1260 cm^{-1}, -Si-O-Si at 1186 cm^{-1}; ^{1}H-NMR ($CDCl_3$, ppm) peaks at (δ 0.1(s, $SiC\underline{\mathbf{H}}_3$), 0.5 (t, $\text{-}C\underline{\mathbf{H}}_2Si$), 0.86 (t, $\text{-}C\underline{\mathbf{H}}_3$), 1.32 (m, $\text{-}C\underline{\mathbf{H}}_2CH_2Si$) 1.55 (m, $\text{-}C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2$ CH_3), 2.4-2.6 (m, $\text{-}C\underline{\mathbf{H}}_2\text{-}N\text{-}$), 3.4 (m, $\text{-}C\underline{\mathbf{H}}_2OC\underline{\mathbf{H}}_2(CH_2)_2Si$) and 3.57 (d, $CH(OH)C\underline{\mathbf{H}}_2Cl$), 3.85 (m, $\text{-}C\underline{\mathbf{H}}(OH)$)).

3-Chloro, 2-hydroxypropyl, methyl, n-propyl quaternary amino PDMS (QPDMS) (5): clear, viscous, pale yellow oil, 91% yield, FT-IR peaks due to CH-OH at 3407 cm^{-1}, $Si\text{-}CH_3$ at 1260 cm^{-1}, -Si-O-Si at 1186 cm^{-1}; ^{1}H-NMR peaks at (δ 0.1(s, $SiC\underline{\mathbf{H}}_3$), 0.5 (t, $\text{-}C\underline{\mathbf{H}}_2Si$), 0.86 (t, $\text{-}C\underline{\mathbf{H}}_3$), 1.32 (m, $\text{-}C\underline{\mathbf{H}}_2CH_2Si\text{-}$), 1.55 (m, $\text{-}C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2$ CH_3), 3.45 (m, $\text{-}CH^{2}$ $\text{-}N^{+}$) and 3 .57 (d, $CH(OH)C\underline{\mathbf{H}}_2Cl$), 3.85 (m, $\text{-}C\underline{\mathbf{H}}(OH)$)). Molecular weight calculated from ^{1}H-NMR was 1379.

Synthesis of Starch-g-Quaternary Amino PDMS Copolymer (SQPDMS) (6)

100 mL of acid solution (7 ml 35% HCl in 100 mL water) was added to 50 g of tapioca starch and the mixture was stirred at 50°C for 20 hours. After the reaction, the pH was adjusted to 7 and the degraded starch was filtered off, washed with 100 mL distilled water each time, and dried at 110°C.

2 g of dry degraded starch was placed in a two-necked flask and 20 mL of distilled water was added to it. The pH of the mixture was adjusted to 11.5 using 3% aqueous NaOH solution and QPDMS (0.2, 0.4 or 0.8 g) in 10 mL water was added to the alkaline solution of starch. The reaction mixture was stirred at 80°C for 20 hours and the pH was maintained at 11.5 throughout the

reaction. The reaction mixture was then cooled to room temperature and the pH was adjusted to 5.7. The pale yellow solution was filtered to remove trace suspended particles. The aqueous filtrate was collected and the product was isolated by distilling off water under vacuum. The crude product was washed with 20 mL ether each time to remove the unreacted QPDMS. The product was dried and characterized by FTIR and ^{1}H-NMR.

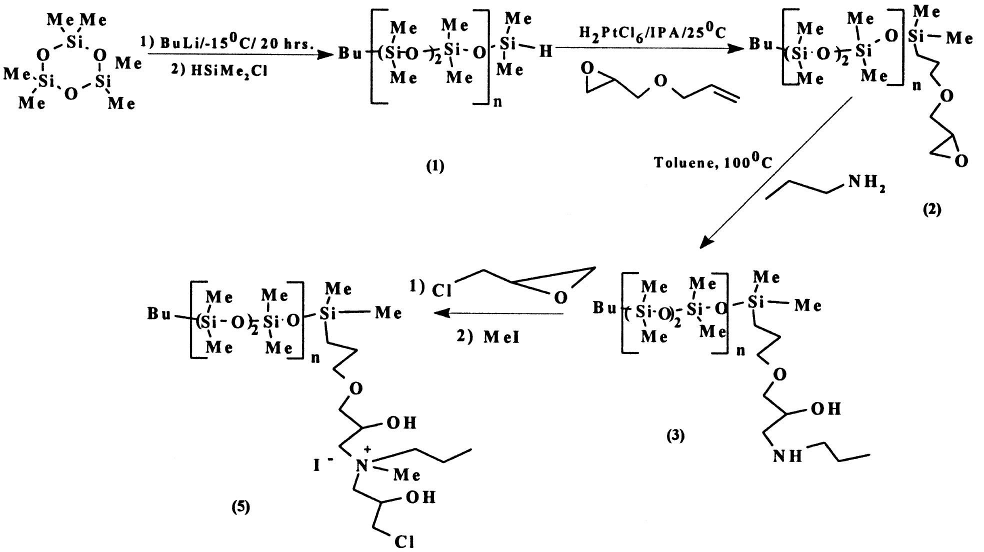
Product Characteristics

Pale yellow solid, 74% yield, FTIR peaks due to at 3600-3300 cm^{-1} (broad hump due to –OH groups in starch), $Si-CH_3$ at 1260 cm^{-1}, -Si-O-Si at 1186 cm^{-1}; ^{1}H-NMR (D_2O, ppm) peaks at (δ 0.1 (s, $SiC\underline{\mathbf{H}}_3$), 0.5 (t, $-C\underline{\mathbf{H}}_2Si$), 0.86 (t, $-C\underline{\mathbf{H}}_3$), 1.32 (m, $-C\underline{\mathbf{H}}_2CH_2Si-$), 1.55 (m, $-C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2 CH_3$), 3.2-4 (complex, $-C\underline{\mathbf{H}}_2OC\underline{\mathbf{H}}_2(CH_2)_2Si$, $C\underline{\mathbf{H}}_2-N^+$, $CH(OH)C\underline{\mathbf{H}}_2-O$, $-C\underline{\mathbf{H}}(OH)$, and $C\underline{\mathbf{H}}_2-O$ linkages in starch).

RESULTS AND DISCUSSION

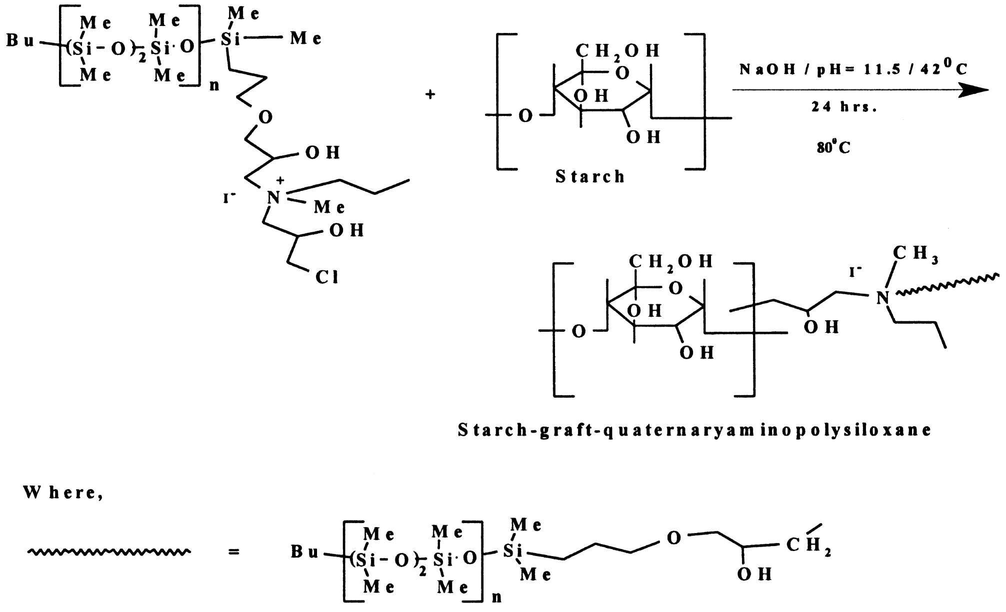
Starch can be made surface-active by introducing a linear hydrocarbon unit and quaternary amino group in it. Water soluble, cationic starch derivatives [8, 9] have been synthesized by the reaction of 3-chloro-2-hydroxypropyl, trimethyl ammonium chloride or 3-chloro-2-hydroxypropyl, dimethyl, dodecyl quaternary ammonium salt (DDCQA) with starch under alkaline conditions. Introduction of PDMS and quaternary amino group in starch is expected to improve the surface-active properties. This is due to higher surface activity of quaternary amino siloxanes [10] than hydrocarbon surfactant e.g. linear alkyl benzene sulphonate (LAS) and 3-chloro-2-hydroxypropyl, dodecyl quaternary ammonium chloride (DDCQA). The methylene groups in the hydrocarbon surfactants have higher surface energy [11] as compared to the dimethyl groups on the PDMS backbone [12].

This paper focuses on the introduction of quaternary amino terminated PDMS chain in starch molecule to obtain water soluble starches, with higher surface activity than the cationic starch containing hydrocarbon units. In order to synthesize water-soluble starch-g-quaternary amino PDMS (SQPDMS), 3-chloro-2-hydroxypropyl, methyl, n-propyl quaternary amino PDMS (QPDMS) (5) was synthesized and subsequently reacted with starch. Reaction Scheme 1 describes the synthesis of 3-chloro-2-hydroxypropyl, methyl, n-propyl quater-



Scheme 1. Synthesis of 3-chloro-2-hydroxypropyl, methyl, n-propyl, quaternary amino PDMS (QPDMS).

nary amino PDMS (QPDMS) (5). Silanic hydrogen terminated PDMS was synthesized by initiating the polymerization of hexamethylcyclotrisiloxane (D_3) using n-butyllithium followed by terminating the living PDMS with chlorodimethylsilane (Me_2HSiCl). This was subsequently hydrosilated with allyl glycidyl ether in the presence of hexachloroplatinic acid to give epoxy terminated PDMS which on reaction with n-propylamine gave n-propyl aminohydroxy PDMS. This was on further reaction with epichlorohydrin followed by methyliodide gave 3-chloro-2-hydroxypropyl, methyl, n-propyl quaternary amino PDMS (QPDMS) (5). The product was characterized using FTIR and ^{1}H-NMR. As indicated in scheme 2, QPDMS (5) was further reacted with degraded starch [13]. (synthesized as explained in the experimental section) at 80°C for 20 hours by maintaining the pH at 11.5 throughout the reaction. The reaction mixture was filtered at pH 5.7. The product was separated from the aqueous filtrate by distilling off water under vacuum and washed several times with ether to remove unreacted QPDMS. Table 1 indicates %N and %Si in SQPDMS, which is obtained by reacting different amounts of QPDMS with starch. The ratio of starch/siloxane was calculated from the amount of % nitrogen obtained[14]. ^{1}H-NMR of product (5) and (6) are shown in Figures 1 and 2. ^{1}H-NMR spectrum of SQPDMS



Scheme 2. Synthesis of starch-g-quaternary amino PDMS copolymer (SQPDMS).

shows peak at (δ 0.1 is due to $Si\text{-}C\underline{H}_3$ and peaks at δ 3.2- 4 are due to $-C\underline{H}_2\text{-}O\text{-}C\underline{H}_2\text{-}$, $\text{-}C\underline{H}_2\text{-}N^+$ and anhydroglucose units.

Surface-Active Property of Cationic Starch-g-Quaternary Amino PDMS Copolymer (SQPDMS)

The cationic starch-g-quaternary amino PDMS copolymer (SQPDMS) (shown in Figure 4a), obtained by reaction with QPDMS (shown in Figure 3a) is

TABLE 1. Elemental Analysis of SQPDMS which is Obtained by Reacting Different Amounts QPDMS with Starch

SQPDMS Sample No.	% N	% Si	Surface tension of SQPDMS (mN/m)
1	0.0195	1.57	25.5
2	0.027	2.26	23.7
3	0.041	3.44	22.7

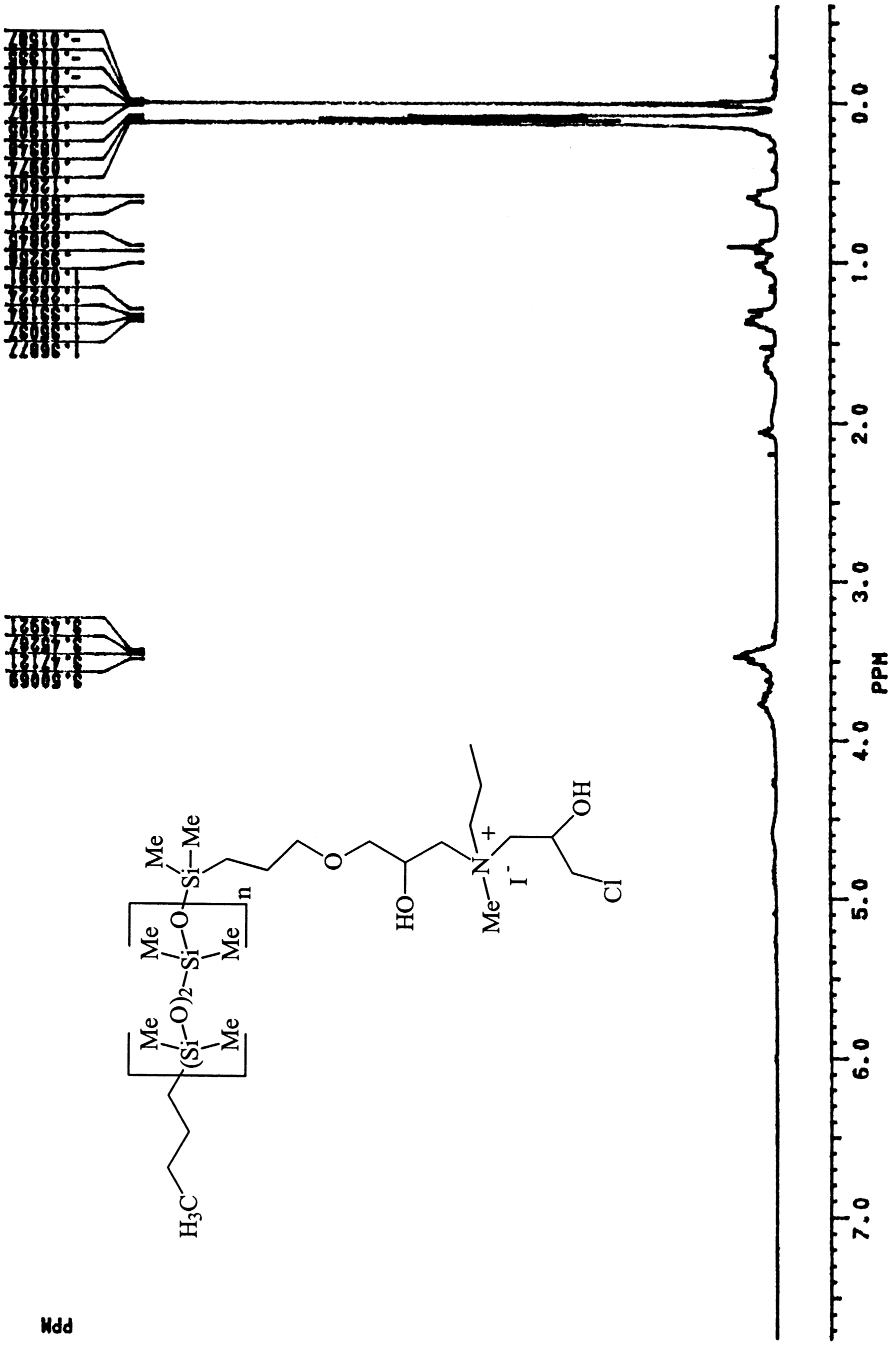


Figure 1. ^{1}H-NMR of 3-chloro-2-hydroxypropyl, methyl, n-propyl quaternary amino PDMS (QPDMS) (5) in CD_3COCD_3.

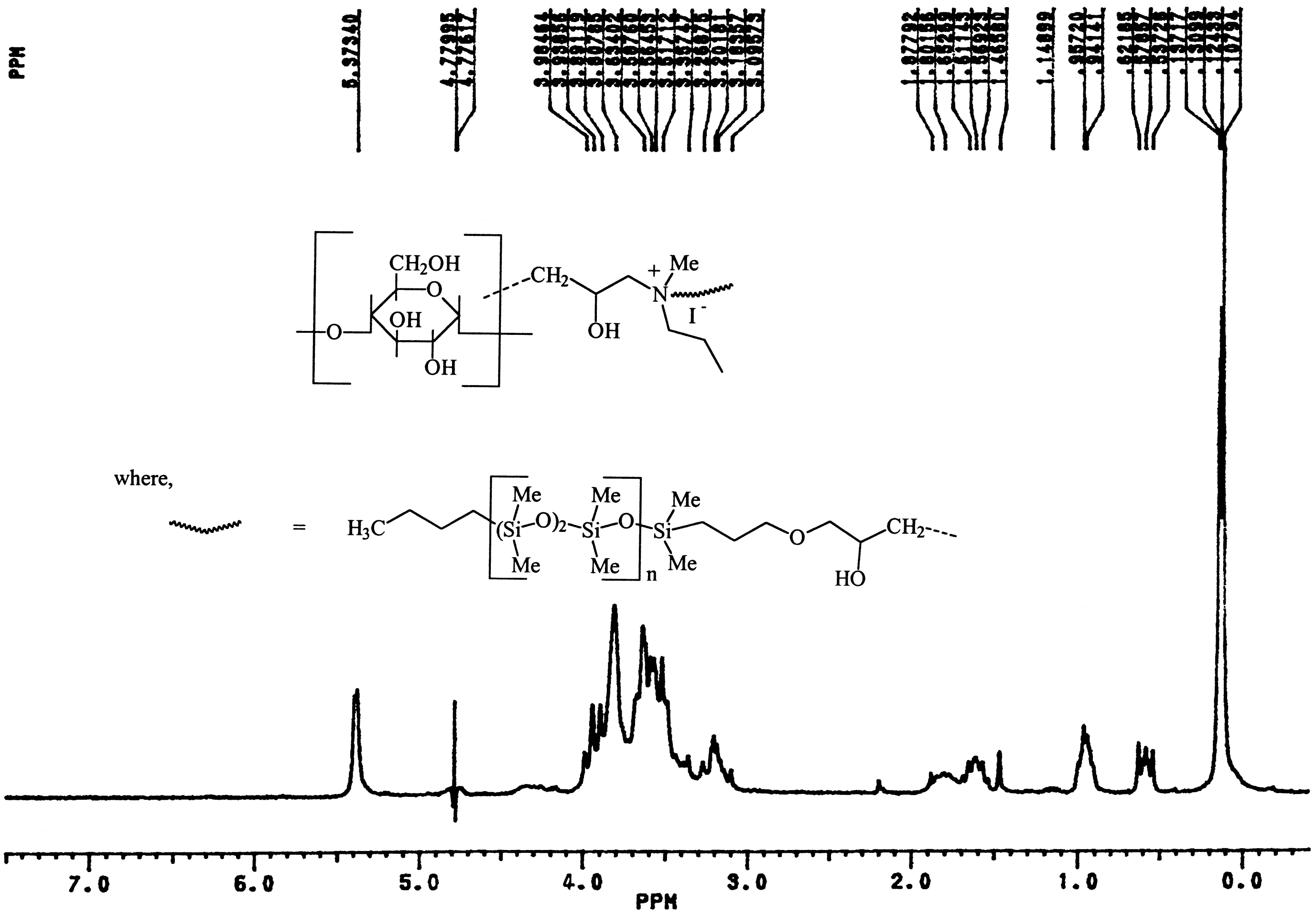


Figure 2. ^{1}H-NMR of starch-g-quaternary amino PDMS (SQPDMS) copolymer in D_2O after solvent suppression at δ 4.78.

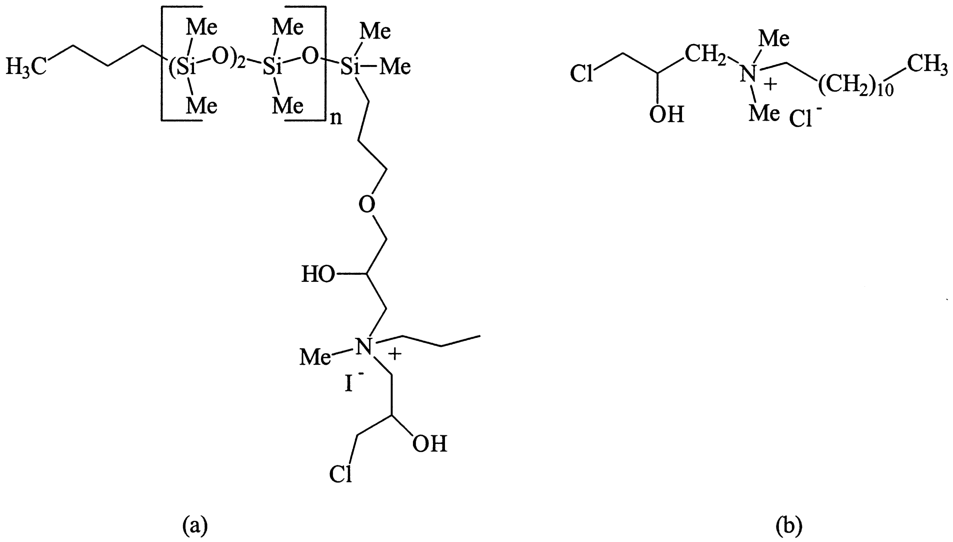

(a) (b)

Figure 3. a) QPDMS and b) DDCQA.

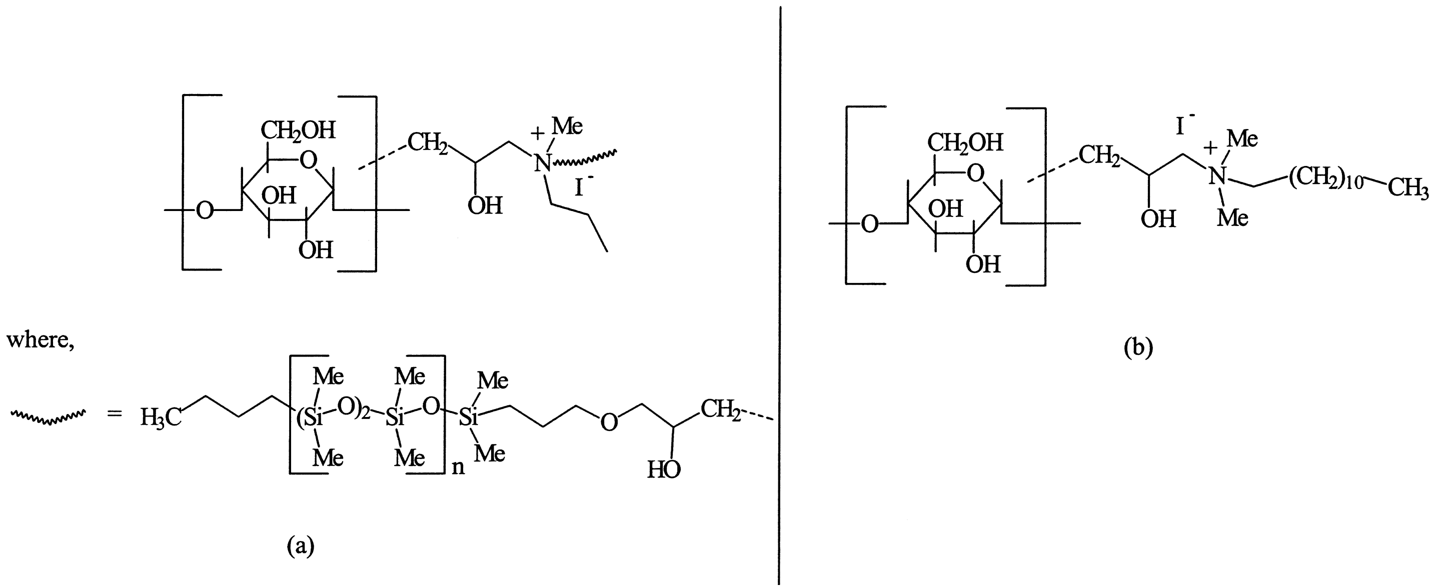
more surface active than cationic starch containing hydrocarbon unit (shown in Figure 4b), obtained by reaction with DDCQA (shown in Figure 3b). As shown in Figure 5, cationic starch containing hydrocarbon unit shows reduction in surface tension of water to 40 mN/m (curve 4) while SQPDMS shows surface tension 22-24 mN/m (curve 1,2,3). The lowering in surface tension increases with increase in %Si in the graft copolymer.

CONCLUSION

Introduction of quaternary amino PDMS moiety into starch, gave water soluble cationic graft copolymer of starch having excellent surface-active properties. This was obtained by reaction of 3-chloro-2-hydroxypropyl, methyl, n-propyl quaternary amino PDMS (QPDMS) with degraded starch. The surface-activity was regulated by changing the number of siloxane units in the graft copolymer.

ACKNOWLEDGEMENT

The authors are grateful to Hindustan Research Foundation for the financial support.



(a)

(b)

Figure 4. a) SQPDMS and b) cationic starch containing hydrocarbon unit.

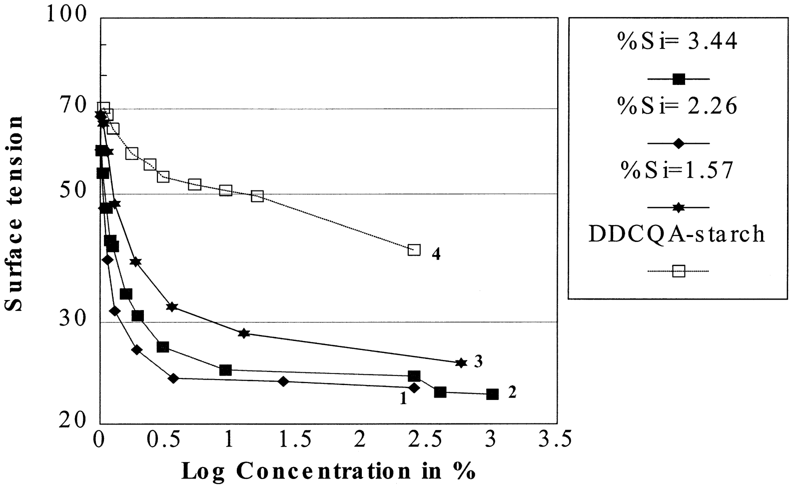


Figure 5. Plot of surface tension(mN/m) vs. concentration in weight % of SQPDMS copolymer (curves 1, 2, 3) and Cationic starch containing hydrocarbon (curve 4).

REFERENCES

[1] H. Gruber, E. Mossl, H. Kazemi, and G. Greber, *Angew. Makromol. Chem., 202/203*, 213 (1992).

[2] V. von Braunmuhl and R. Stadler, *Macromol. Symp., 103*, 141 (1996).

[3] V. von Braunmuhl and R. Stadler, *Polymer, 39(8-9),* 1617 (1998).

[4] H. L. Frush and H. S. Isbell, *Methods Carbohydr. Chem, 2*, 14 (1963).

[5] W. N. Emmerling and B. Pfannemuller, *Carbohydr. Res., 86*, 321 (1980).

[6] U. Takashi, T. Shigeyuki, N. Masahiro, H. Norio, and O. Norishige, J.P. patent: 62218401.

[7] A. Juergen, H. Horst, K. Ute, H. Van der Maas, and H .P. Suerken, Ger. Offen. DE: 3310088.

[8] *Modified Starches: Properties and Uses*, by O. B. Wurzburg, CRC Press, Inc.

[9] E. F. Paschall, U.S. Patent: 2,876,217 (1959).

[10] Ashish Vaidya and V. G.Kumar, *J. Macromol. Sci., Pure & Appl. Chem., 36(4)* (1999).

[11] E. G. Shafrin and W. A. Zisman, *J. Phy. Chem., 64*, 523 (1960).

[12] M. J. Owen, *Ind. Eng. Chem, Prod. Res. Dev., 19*, 97 (1980).

[13] P. Erkki, S. Tapani, A. Karin, and P. Kaisa, *Starch/Staerke, 44(2),* 64 (1992).

[14] *Vogel's Textbook of Quantitative Inorganic Analysis*, Fourth Edition, p. 312.

Received June 20, 1998
Revision received April 10, 1999