

ARTICLES

A Novel Luminescent Functionalized Siloxane Polymer

Madhavan P. Vinod,^{*,†,‡,§} Detlef Bahnemann,[†] Pattuparambil R. Rajamohanam,[‡] and Kunjukrishnan Vijayamohanam[‡]

Physical Chemistry Division, National Chemical Laboratory, Poona 411 008 India and
Institut fuer Technische Chemie, Universität Hannover, Callinstrasse 3, D-30167 Hannover, Germany

Received: January 1, 2003; In Final Form: May 18, 2003

The simple chemical reaction between acetone and tetrachlorosilane is found to yield a functionalized siloxane polymer that can emit light under normal conditions, if irradiated with a suitable wavelength. In situ multinuclear NMR spectra during various stages of the reaction show the formation of intermediates such as mesityl oxide (MeO), diacetone alcohol (DAA), phorone, isophorone, etc. Thus, the reaction is initiated via a type of self-condensation of acetone in the presence of tetrachlorosilane. The reaction provides a strongly acidic dehydrating atmosphere, which can be generated otherwise only in the presence of a specific catalyst and/or at high temperatures. The reaction of the keto group with SiCl_4 is known to form siloxy-conjugated enes. On the other hand, the fast hydrolysis reaction leads to a siloxane network. Thus various condensation and dehydration reactions lead to a functionalized siloxane polymer with a lot of inherent π -bonded carbon atoms. The gel obtained shows strong room-temperature photoluminescence (PL) with a maxima at 655 nm. The origin of PL is the presence of large amount of delocalized π -electrons in the system, which can enhance the radiative recombination of holes and electrons, which is further supported by the ESR spectra of the gel.

1. Introduction

Although silicon plays a central role in microelectronics, its use in optoelectronics is hampered by the indirect band gap, which is unfavorable for photonic emission. As a result, although most of the optical components such as waveguides, light modulators, and detectors can be made from silicon, the light sources, semiconductor lasers, and light-emitting diodes (LED's) cannot be made from silicon. Since light-emitting silicon can revolutionize photonics by making it all-silicon-technology, many physical and chemical approaches have been attempted to squeeze light from silicon. Two major approaches in making luminescent silicon are creating nanopores on silicon by chemical or electrochemical etching and by creating additional radiative recombination centers. Among them porous silicon is particularly interesting, because of its unique aspects regarding spatial confinement and dimensionality.^{1–4} Other small silicon particles including colloidal silicon^{3d} and ultrafine silicon⁵ are also studied for their light-emitting properties. Chemical modification of silicon to modulate its optical properties has also been attempted.^{3f} For example, emission of blue light from the hydrogenated amorphous silicon carbide thin film was observed.⁶ Several organosilicon compounds have been synthesized in which regular alternative arrangements of organosilicon groups and π -electron-containing units are present in the backbone.⁷ These polymers have been synthesized by using

various chemically different silicon centers performed by Grignard reactions or by hydrosilylation of hydrocarbons with silanes.⁸ One recent approach involving the chemical synthesis of such light-emitting polymers is using the reaction between various organic acids and silicon sources such as tetraalkoxysilane.^{3c} These organosilicon polymers remarkably combine the diverse properties of inorganic backbone and organic polymers. Organosilicon polymers are also important as precursors for high-tech ceramics such as carbides and nitrides of silicon.⁹

Synthesis and characterization of various siloxane polymers have received great deal of attention during recent years.⁹ Cyclic and linear siloxanes can be made via the hydrolysis and condensation of chlorosilanes. Organofunctional siloxanes are a broad class of polymers in which the conventional polysiloxanes are modified by incorporating a variety of chemically reactive groups along the siloxane chain. Organosiloxane polymers are unique because of their wide range of properties and variety of structural forms. Organic functional groups influence the material to the extent that siloxanes with unexpected new properties can be produced. Organofunctional siloxanes are widely used in many commercial applications. For example amino-functional siloxanes are widely used in textiles and household care products. Other applications of organosiloxane polymers include elastomeric materials, photoresists, catalysis, liquid crystalline polymers, and polyelectrolytes. The versatility of siloxane polymers is attributed to the characteristic of the siloxane backbone. In addition, the ionic character of the siloxane backbone imparts very good thermal and oxidative stabilities for these polymers.

The reaction between acetone and tetrachlorosilane is of historical interest.¹⁰ Although a simple and straightforward reaction, it is not widely studied. It is known that when acetone

* To whom correspondence should be addressed. Current address: Department of Chemistry and Biochemistry, University of Missouri at St. Louis, St. Louis, Missouri. Fax: 314-512-5346. E-mail: vinodm@msx.umsl.edu.

[†] Universitaet Hannover.

[‡] National Chemical Laboratory.

[§] Alexander Von Humboldt fellow.

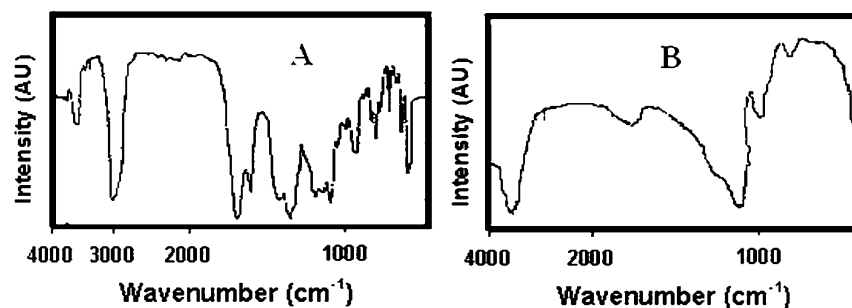


Figure 1. (A) IR spectrum of the reaction mixture during the early stages of the reaction between acetone and tetrachlorosilane recorded in the form of a thin film on a CsBr plate. (B) IR spectrum of the completely cross-linked gel recorded as a pressed KBr pellet.

is mixed with tetrachlorosilane, a yellow color develops slowly which ultimately turns into dark brown and finally to a black solid. Some investigators identified the intermediates such as mesityl oxide (MeO), diacetone alcohol (DAA), phorone, isophorone, etc.,¹⁰ SiCl_4 being a Lewis acid catalyzing the usual aldol condensation of acetone. However, the reaction should be carried out under conditions such that complete conversion of SiCl_4 to silica and hydrochloric acid is not affected. Reactions of tetrachlorosilane with other organic solvents are also known; with dimethyl formamide it forms a siloxane, with benzaldehyde it forms a chlorosiloxane, with ether it forms ethoxysilane, and with amines it forms molecular addition products.¹⁰

Several years ago we reported the luminescent properties of silicon-based light-emitting gels obtained from the reaction between acetone and tetrachlorosilane.¹¹ However, the mechanism of the reaction and the nature of the gel formed are still unknown. In the present study, we report the mechanism of the gel formation and chemistry of the light emission obtained using various physicochemical methods. We monitored the reaction between acetone and tetrachlorosilane using various spectroscopic methods and observed that it leads to a functionalized siloxane polymer that can emit light at room temperature if irradiated with a suitable wavelength. The reaction is followed by multinuclear NMR spectroscopy and ultraviolet (UV) visible spectroscopy. The reaction mixture and the gel are also characterized by infrared (IR) spectroscopy. Radical sites in the completely cross-linked gel are identified using electron spin resonance spectroscopy (ESR). The redox centers in the gel before cross-linking have been identified using cyclic voltammetry (CV).

2. Materials and Methods

The reaction between acetone and tetrachlorosilane has been carried under an argon atmosphere in a sealed container.¹¹ The rate of the reaction and nature of the gel was found to depend on the type of acetone and tetrachlorosilane used. In this study AR grade acetone (Aldrich) and AR grade tetrachlorosilane (Aldrich) were used. HCl gas produced was removed periodically using a syringe. It took about 30 days to form a completely cross-linked gel, which is a black solid. Anal. Found of the solid: C, 38.92%; H, 5.4%; O, 24.7%; Si, 13.5%; Cl, 17.5%.

The IR spectra of the reaction mixture were recorded in the form of a thin film on a CsBr plate. IR spectra of the completely cross-linked gel were obtained in the form of pressed KBr pellets. The IR spectra of the samples were recorded in a Nicolet 60 XB spectrometer in the range between 400 and 4000 cm^{-1} . The UV spectra of the reaction mixture in benzene were recorded in a Shimadzu (Model UV 2101 PC) spectrophotometer in the wavelength range 200–700 nm. The PL spectra were recorded at room temperature using an argon ion laser (488 nm

lines) as an excitation source, monochromator grating of 1 μm , with L_p filter 0.515 μm , slit 2 mm, and a silicon photodiode with a lock-in-amplifier as the detector. The ESR spectra of the sample were recorded at room temperature using a JEOL Model ESR spectrometer.

Cyclic voltammetry experiments were carried out in 0.1 M solution of tetrabutylammonium tetrafluoroborate (TBFAB) in acetonitrile using a platinum electrode of geometrical area 0.02 cm^2 as working electrode in a three-electrode-single-compartment cell with a saturated calomel reference electrode and platinum foil counter electrode in an argon atmosphere. All the experiments were conducted using a PAR 173 potentiostat coupled with a PAR 175 function generator.

All the NMR measurements were made on a Bruker MSL 300 NMR spectrometer operating at 300, 75.47, and 56.9 MHz, respectively for ^1H , ^{13}C , and ^{29}Si nuclei. The in situ measurements were carried out in a standard 10 mm broadband probe at ambient temperature (298 K). The neat reaction mixture was taken in a 10 mm outer diameter standard NMR tube, and the ^{13}C and ^{29}Si NMR spectra were followed with time for about three weeks. The field-frequency lock was maintained by means of a D_2O capillary tube placed inside the 10 mm NMR tube. The chemical shifts were measured with respect to external dioxane in D_2O for ^{13}C (67.8 ppm from TMS) and external TMS (0 ppm) for ^{29}Si . The ^1H spectra were obtained by dissolving the reaction mixture in CDCl_3 .

For the solid state ^{13}C and ^{29}Si measurements, the finally powdered reaction product was packed in a 7 mm zirconia rotor and spun at 3–4 kHz. The CP/MAS spectra were recorded under Hartmann–Hahn match condition using contact times of 1 and 2 ms for ^{13}C and ^{29}Si , respectively. The match conditions were calibrated using a spinning sample of adamantane for ^{13}C and hydrolyzed tetraethylosilicate (TEOSi) for ^{29}Si . The chemical shifts were referred with respect to the CH_2 carbon of adamantane (+28.7 ppm from TMS) and neat TEOSi (−82.4 ppm from TMS).

3. Results and Discussion

The IR spectra of the reaction mixture recorded as a thin film in a CsBr plate during early stages of the reaction is shown in Figure 1A. The major IR peaks observed are at (in cm^{-1}) 3498, 3403, 2980, 2934, 1710, 1690, 1615, 1460, 1383, 1206, 1150, 1110, 1070, 1020, 928, 903, 860, 820, 798, 740, 700, 662, and 622. The peaks above 3000 cm^{-1} correspond to O–H stretching vibrations. Peaks at 2980 and 2934 cm^{-1} correspond to C–H symmetric stretching vibrations. Peaks at 1710 cm^{-1} correspond to the C=O stretching vibration. The peak at 1690 cm^{-1} corresponds to a C=C vibration. The 1460 and 1383 cm^{-1} peaks are due to antisymmetric C–H stretching vibrations. Peaks at 1206 cm^{-1} correspond to symmetric C–H deformation. Peaks

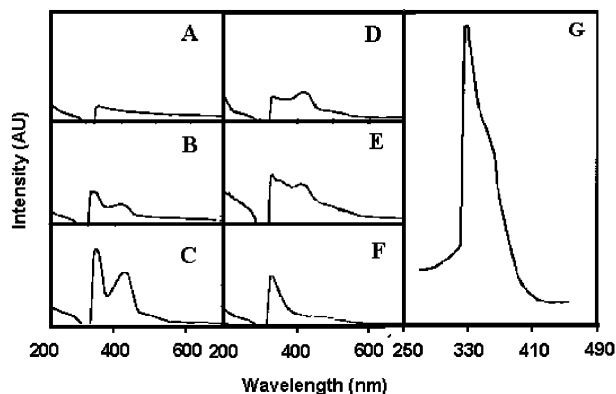


Figure 2. UV-visible spectra of the reaction mixture during various stages of the reaction: (A) 0 h; (B) 1 h; (C) 2 h; (D) 5 h; (e) 8 h; (f) 24 h; (g) completely cross-linked gel obtained by swelling the gel in Nujol and recorded against a Nujol background.

at 1070–1020 cm^{-1} correspond to SiOSi stretching vibrations, and peaks at 1150–1110 cm^{-1} correspond to SiOC stretching vibrations, whereas, the SiOC stretching vibrations are observed at 928 and 903 cm^{-1} . The corresponding asymmetric SiOSi stretching modes are observed at 740 and 700 cm^{-1} . The Si–Cl stretching vibrations are observed at 662 cm^{-1} . Thus the IR spectra indicates the formation of SiOC and SiOSi during the early stages of the reaction and lots of C=C bonds formed during the reaction. Peaks correspond to Si–H stretching vibration at 2160 cm^{-1} and Si–Si stretching vibration at 519 cm^{-1} are particularly absent in the IR spectrum of the reaction mixture.

The IR spectrum of the completely cross-linked gel is recorded in the form of a pressed KBr pellet is shown in Figure 1B. The spectrum shows only few major peaks at 3395, 2465, 1645, 1066–1207, 960, and 798 cm^{-1} . Among these, the peak at 3395 cm^{-1} corresponds to an O–H stretching vibration while the peak observed at 2465 cm^{-1} is known in organosilicon polymers as Si surface defects. The 1645 cm^{-1} peak corresponds to C=C stretching vibration. Peaks were observed in the entire region of 1000–1200 cm^{-1} with maxima at 1066 and 1207 cm^{-1} corresponding to the SiOSi and SiOC stretching vibrations. The peak observed at 960 cm^{-1} is assigned to the Si–OH stretching vibration. Peaks corresponding to Si–H stretching vibration (2150 cm^{-1}) and Si–Si stretching vibrations (519 cm^{-1}) are particularly absent in the spectrum. Thus IR spectra of the completely cross-linked gel obtained from the reaction between acetone and tetrahalorosilane is of a functionalized siloxane polymer with infinite chain length. In addition, the siloxane polymer also contains lots of inherent π -electrons in the form of C=C bonds in the backbone.

Interesting color changes observed during the reaction help in the in situ monitoring of the reaction rate using UV–visible spectroscopy. Both acetone and tetrahalorosilane are colorless, and therefore, an investigation of the UV–visible absorption as the reaction proceeds will give valuable information about the mechanism of the reaction. The UV–visible spectrum of the reaction mixture (Figure 2) shows a peak at 356 nm immediately after mixing the reactants. After 1 h the intensity of the peak increases, and interestingly, an additional peak is slowly seen to emerge at 411 nm. These two peaks are easily distinguishable in the spectra obtained after 2 h. After reaching the maximum value, the intensities of both the peaks are found to be decreasing, and after 24 h only the one peak is observed at 333 nm. The 333 nm absorption peak is matched well with that observed for diacetone alcohol. The UV–visible spectra of the gel after cross-linking shows only this peak.

TABLE 1: Solid-State NMR Data for the Completely Cross-Linked Gel

^{13}C NMR peaks		^{29}Si NMR peaks	
chemical shifts	assignment	chemical shifts	assignment
210.6	C=C–O–Si	100.4	SiOC
124.4	C=C	109.8	SiOSi
75.5	C–C–O		
71.4	C–C–O		
50.8	C–C–O–Si		
30.3	H ₃ C–C		

Normal alkyl siloxanes are not UV active, and any absorption of even functionalized siloxanes above 220 nm is not known.¹³ The first peak observed at 356 nm is due to the $n\text{--}\pi^*$ transition in conjugated ketones. The $n\text{--}\pi^*$ transition in mesityl oxide is observed at 305 nm. The shift in wavelength observed for siloxy-conjugated ketones compared to the native ketones is due to the conjugation from the siloxane group. Due to its 49% ionic character, the Si–O bonds influence the $n\text{--}\pi^*$ transitions in the ketones. The peak observed at 411 nm is due to the $n\text{--}\pi^*$ transition in diacetone alcohol. This peak vanishes slowly as the compound is transformed to phorone. The peak observed at 333 nm is due to the siloxy-conjugated dienes and triens formed as the end product of the condensation reaction. Interestingly, polysilanes with a structure of --C(=O)--SiR_3 show a $n\text{--}\pi^*$ transition at 365 nm, while on UV irradiation the peak is shifted to 330 nm.^{9b} This shift in wavelength was attributed to the C–O–Si bond formed during UV irradiation. In the present reaction, a similar C–O–Si bond is forming during the condensation reaction.

The progress of the reaction between acetone and silicon tetrachloride was monitored through ^{13}C and ^{29}Si NMR spectroscopies, and the data for the completely cross-linked gel are summarized in Table 1. The ^{13}C spectra at various stages of the reaction is shown in Figure 3. The ^{13}C spectrum of the neat reaction mixture immediately after mixing shows the presence of only acetone as evident from the CH_3 (31 ppm) signal and the C=O signal at 205.9 ppm.

Two new signals at 101.2 and 36.5 ppm developed slowly with time and were quiet visible after 15 h. These signals are from a quaternary carbon and a methyl carbon respectively (from the DEPT spectrum). The former signal is typical of $\text{--O--C(Me}_2\text{)--O--}$ type of environment. A trace amount of water is essential for the reaction, as completely dry acetone under inert atmosphere fails to undergo any reaction with SiCl_4 even after few weeks. Hence the sequence of reaction as shown in Scheme 1 can be envisaged.

The signals at 101.2 and 36.4 ppm correspond to the two carbons of the intermediate $(\text{CH}_3)_2\text{C(OSiCl}_3)_2$. Moreover, the formation of $\text{Cl}_3\text{SiO--}$ species is also confirmed from the ^{29}Si NMR spectra (Figure 4), which showed two signals at -20.7 and -47.8 ppm, corresponding to $\text{Cl}_3\text{SiO--}$ and SiCl_4 . Development of additional signals at 205 (carbonyl), 68 (quaternary carbons), 58 (CH_2), and 33 ppm (CH_3) were also noticed at longer times (after 11 days). The nature of signals and the chemical shifts corresponds to the formation of DAA, which can be formed by an aldol type of condensation of acetone molecules. The signal intensity of DAA also builds up with time.

On completion of the reaction, a blackish brown gel is obtained, and ^{29}Si NMR spectra of it did not show the presence of any soluble silicone species. On the other hand, a ^{13}C spectrum of this showed the presence of many reaction products, some of which contain many sp^2 carbons as well (120–130 ppm). Though these products are not isolated, it is reasonable

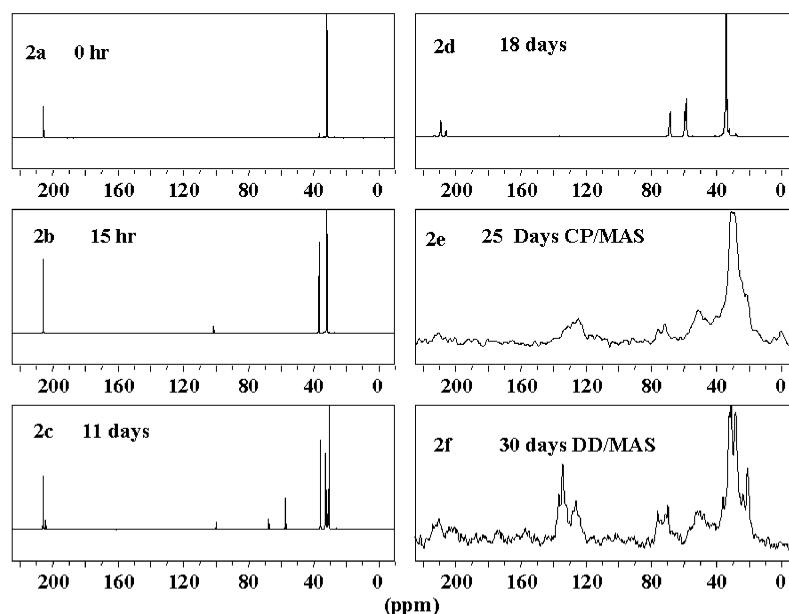
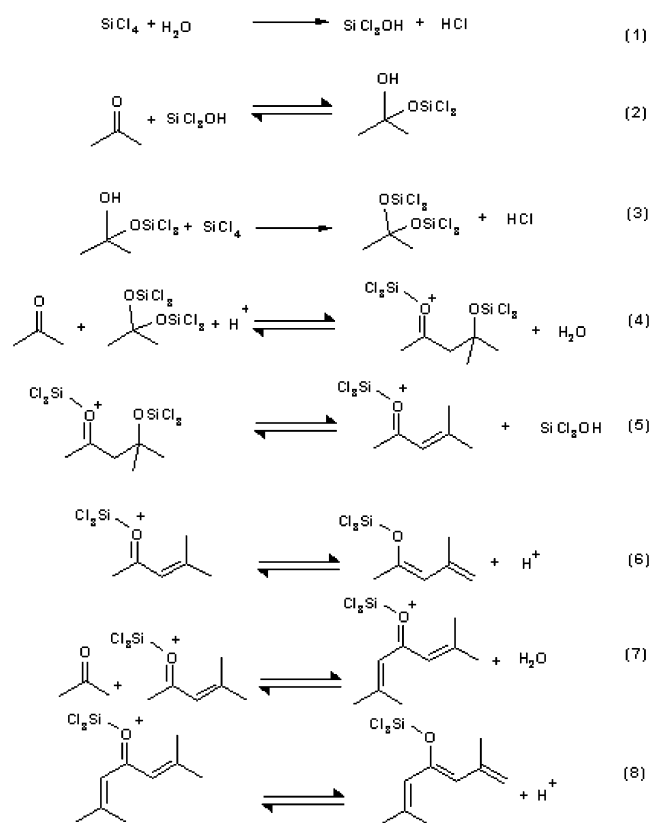


Figure 3. ^{13}C NMR spectra recorded at various stages of the reaction between acetone and tetrachlorosilane

SCHEME 1: Various Steps Observed during the Reaction between Acetone and SiCl_4



to presume that these are formed by either from DAA or different condensation products of acetone itself. Some of these products are likely to be mesityl oxide, phorone, isophorone, etc.¹⁰ It is interesting to note that ^{13}C CP/MAS spectrum of the product obtained closely resembled that obtained for the reaction products of acetone on zeolites.¹⁵ The solid-state CP/MAS and DD/MAS spectra of the dried gel are also in agreement with this observation. The solid-state ^{29}Si CP/MAS spectrum indicated the presence of SiOH (Q_3), $\text{Si}(\text{OH})_2$ (Q_2) and $\text{Si}-\text{O}-\text{Si}$ (Q_4) environments for silicon.

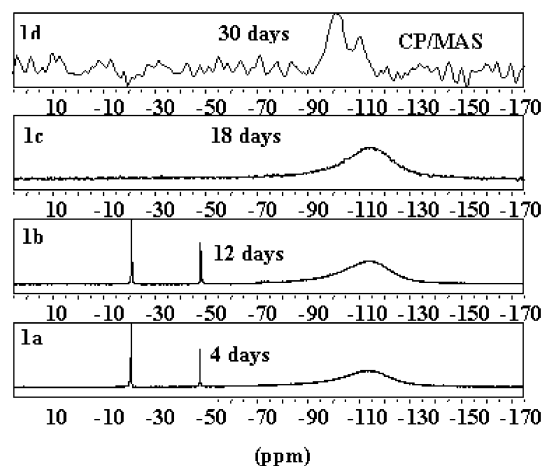


Figure 4. ^{29}Si NMR spectra recorded at various stages of the reaction between acetone and tetrachlorosilane.

Thus from IR, UV, and NMR, the following reaction sequence can be envisaged (Scheme 1). The first thermodynamically possible reaction is the fast hydrolysis of the tetrachlorosilane by trace amount of water present in the system. $\text{Cl}_3\text{SiO}-$ species formed react with acetone and form a siloxy-conjugated ketone. These then undergo the usual condensation reactions of acetone in acidic media involving intermediates such as MeO, DAA, phorone, isophorone, etc. The reaction provides a strongly acidic dehydrating atmosphere, which can be generated otherwise only in the presence of a specific catalyst and or at high temperatures. The reaction of the keto group with SiCl_4 is known to form siloxy conjugated enes.¹⁶

On the other hand, the fast hydrolysis reaction leads to a siloxane network. Thus various condensation and dehydration reaction leads to a functionalized siloxane polymer with lot of inherent π -bonded carbon atoms as shown in Figure 5.

An ESR spectrum of the completely cross-linked gel recorded at room temperature is shown in Figure 6. It gives a strong ESR signal with a narrow bandwidth and a g value of 2.0138. It is interesting to compare this spectrum with that obtained for porous silicon, which shows a narrow peak with a g value of 2.0052 and that of the silyl radical ion, which gives a g value of 2.0032.

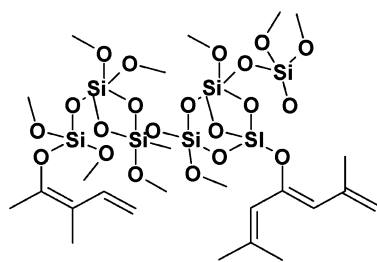


Figure 5. Structure of the luminescent gel obtained from the reaction between acetone and tetrachlorosilane using various spectroscopic method (IR, UV, NMR). The gel is a black solid with trapped hydrochloric acid formed during the condensation reaction. In an inert atmosphere, it took about 1 month to get a completely cross-linked gel.

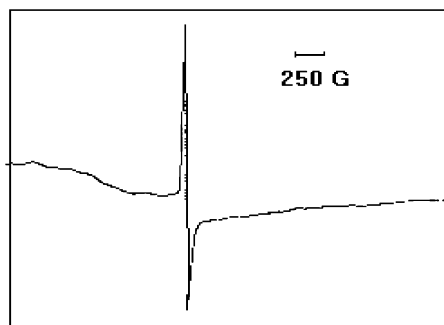


Figure 6. Room temperature ESR spectrum of the completely cross-linked gel obtained from the reaction between acetone and tetrachlorosilane.

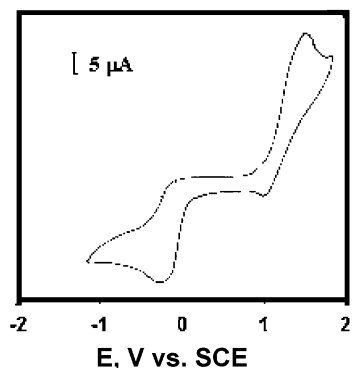


Figure 7. Cyclic voltammogram of the reaction mixture during the end stage of the reaction between acetone and tetrachlorosilane in acetonitrile containing 0.1 M TFAFB as a supporting electrolyte at a scan rate of 500 mV/s.

The ESR activity of the gel is due to the presence of radical sites such as $\text{Si}-\text{O}-\text{Si}^\bullet$ and $\text{Si}-\text{O}-\text{C}^\bullet$ in the polymer backbone. These radical sites are stabilized by the conjugation from the π electrons present in the structure. The role of siloxane network is to provide a stable matrix for these radicals. Thus the ESR spectra of the completely cross-linked gel clearly indicate the presence of stabilized radicals in the system.

Electrochemical properties of the siloxane polymer before cross-linking is studied due to its relevance in electroluminescence and in understanding the mechanism of the luminescence. The cyclic voltammetry of the reaction mixture before cross-linking (in acetonitrile with 0.1 M tetrabutylammonium fluoroborate) is shown in Figure 7.

The CV shows an irreversible n doping at -0.2 V and a nearly reversible p doping at $+1.52$ V. The CV clearly indicates the facile electron transport in the system.

The photoluminescence spectrum of the gel obtained by exciting the sample with argon ion source (488 nm lines) is

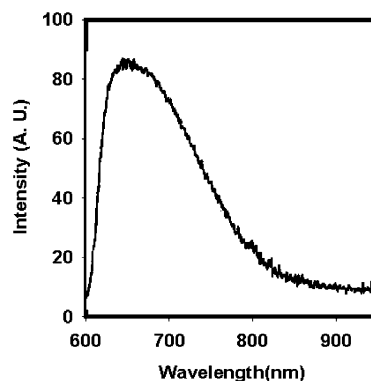


Figure 8. PL spectra of the gel shown in Figure 1, recorded at room temperature using an argon ion laser (488 nm lines) as an excitation source, monochromator grating of $1\ \mu\text{m}$ with L_p filter $0.515\ \mu\text{m}$, slit 2 mm, and a silicon photodiode with a lock-in-amplifier as the detector.

shown in Figure 8. The spectrum shows a broad peak with a maximum at 655 nm. The emission energy obtained from the PL spectrum is 1.89 eV. The UV-visible spectra give a band gap of 3.72 eV.

The origin of photoluminescence in the gel is due to the presence of large amounts of π -bonded carbon attached to the siloxane groups. The siloxyhexatriene groups can stabilize the electron hole pair originating from the irradiation and facilitate their radiative recombination. Additional evidence of such radical formation is obtained from the ESR spectra of the gel. In the gel, there is also a lot of trapped hydrochloric acid formed during the condensation reaction. The presence of hydrochloric acid is known to enhance the luminescence properties of porous silicon.¹⁷ The reversible p-doping observed in the cyclic voltammetry of the gel indicates the facile electron transfer in the system. The presence of conjugated π -electrons in the siloxane matrix creates additional radiative recombination centers, and a visible photoluminescence can be obtained if irradiated with suitable wavelength.

4. Conclusions

In conclusion, reaction between acetone and tetrachlorosilane is found to form siloxy-conjugated hexatriene. The various spectroscopic methods gives evidence of formation of DAA, MeO and phorone during various stages of the reaction. The gel obtained shows strong room-temperature photoluminescence with a maximum at 655 nm. The mechanism of PL is attribute to the presence of large amount of delocalized π -electrons in the system, which can enhance the radiative recombination of holes and electrons. This is further supported by the ESR activity of the gel. Two interesting applications of the reaction are found in the literature. The reaction of acetone with the Si(III) surface at $750\text{--}900\ ^\circ\text{C}$ produces SiC islands.¹⁸ In another application, addition of acetone to an nSi photoelectrochemical cell generates a high open-circuit voltage, high short-circuit photocurrent, and improved overall efficiency of the solar cell.¹⁹

Acknowledgment. The authors acknowledge financial support from the Council of Scientific and Industrial Research, New Delhi, India, and the Alexander von Humboldt Foundation, Germany, for postdoctoral fellowship to M.P.V..

References and Notes

- (1) (a) Brus, L. E.; Szajowski, P. F.; Wilson, W. L.; Harris, T. D.; Schuppler, S.; Citrin, P. H. *J. Am. Chem. Soc.* **1995**, *117*, 2915–2922. (b) Nirmal, M.; Brus, L. *Acc. Chem. Res.* **1999**, *32*, 407–414. (c) Brus, L. *J. Phys. Chem.* **1994**, *98*, 3575–3581 (d) Puritis, T.; Kaupuzs, J. *Ultrafast*

Phenomena in Semiconductors. *Mater. Sci. Forum* **2002**, 384–385, 79–82.

(2) (a) Hamilton, B.; Jacobs, J.; Hill, D. A.; Pettifer, R. F.; Teehan, D.; Canham, L. T. *Nature* **1998**, 393, 443–445. (b) Cullis, A. G.; Canham, L. T.; Calcott, P. D. J. *J. Appl. Phys.* **1997**, 82, 909–965. (c) Canham, L. T.; Cullis, A. G.; Pickering, C.; Dosser, O. D.; Cox, T. I.; Lynch, T. P. *Nature* **1994**, 368, 133–135. (d) Cullis, A. G.; Canham, L. T. *Nature* **1991**, 353, 335–338.

(3) (a) Song, J. H.; Sailor, M. J. *J. Am. Chem. Soc.* **1998**, 120, 2376–2381. (b) Song, J. H.; Sailor, M. J. *J. Am. Chem. Soc.* **1997**, 119, 7381–7385. (c) Green, W. H.; Le, K. P.; Grey, J.; Au, T. T.; Sailor, M. J. *Science* **1997**, 276, 1826–1828. (d) Heinrich, J. L.; Curtis, C. L.; Credo, G. M.; Kavanagh, K. L.; Sailor, M. J. *Science* **1992**, 255, 66–68. (e) Lauerhaas, J. M.; Sailor, M. J. *Science* **1993**, 261, 1567–1568. (f) Song, J. H.; Sailor, M. J. *Comments Inorg. Chem.* **1999**, 21 (1–3 Part A), 69–84.

(4) (a) Wise, M. L.; Sneh, O.; Okada, L. A.; George, S. M. *Surf. Sci.* **1996**, 364 (3), 367–379. (b) Okada, L. A.; Dillon, A. C.; Ott, A. W.; George, S. M. *Surf. Sci.* **1998**, 418 (2), 353–366.

(5) Holmes, J. D.; Ziegler, K. J.; Doty, R. C.; Pell, L. E.; Johnston, K. P.; Korgel, B. A. *J. Am. Chem. Soc.* **2001**, 123, 3743–3748.

(6) Nevin, W. A.; Yamagishi, H.; Yamaguchi, M.; Tawada, Y. *Nature* **1994**, 368, 529–531.

(7) Zybail, C.; Koch, V. P. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 845–848.

(8) (a) Kendrick, T. C.; Parbhoo, B.; Thompson, J. W. *The Chemistry of Organosilicon Compounds*; Patti, S., Rappaport, Z., Eds.; Wiley: New York, 1989; pp 1289–1362.

(9) (a) Segal, D. L. *Br. Cream. Trans J.* **1986**, 85, 184–187. (b) Sifter, D. In *Silicon Based Polymer Science*; Zeigler, J. M., Gordon, F. W., Eds.; American Chemical Society: Washington, DC, 1990; p 565.

(10) (a) Currie, J. N. *J. Am. Chem. Soc.* **1914**, 35, 1061. (b) Trost, W. R. *Can. J. Chem.* **1951**, 29, 877–884. (c) Lanning, F. C.; Moore, M. J. *Org. Chem.* **1958**, 23, 288–291. (d) Zappel, A. *J. Am. Chem. Soc.* **1955**, 77, 4228. (e) Klein, F. G.; Banchemo, J. T. *Ind. Eng. Chem.* **1948**, 48, 1278–86. (f) Myers, A. G.; Kephart, S. E.; Chen, H. *J. Am. Chem. Soc.* **1992**, 114, 7922–7923.

(11) (a) Vinod, M. P.; Vijayamohanan, K. *Appl. Phys. Lett.* **1996**, 68, 81–83. (b) Suresh, S.; Joshi, U. M.; Vinod, M. P.; Pavaskar, N. R.; Vijayamohan, K. *Chem. Mater.* **1997**, 9, 1186–1190.

(12) Isler, O.; et al. *Chim. Acta* **1947**, 30, 1911.

(13) Smith, A. L.; Mihard, J. A. *Anal. Chem.* **1954**, 31, 1174.

(14) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970.

(15) Barich, D. H.; Nicholas, J. B.; Xu, T.; Haw, J. F. *J. Am. Chem. Soc.* **1998**, 120, 12342–12350.

(16) Torok, D. S.; Scott, W. J. *Tetrahedron Lett.* **1993**, 34, 3067–3070.

(17) (a) Prokes, S. M.; Carlos, W. E.; Seals, L.; Gole, J. L. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, 62, 1878–1882. (b) Prokes, S. M.; Glembocki, O. J.; Bermudez, V. M.; Kaplan, R.; Friedersdorf, L. E.; Searson, P. C. *Phys. Rev. B: Condens. Matter* **1992**, 45, 13788–91.

(18) Takami, T.; Ishidzuka, S.; Igari, Y.; Range, H.; Kusunoki, I. *Thin Solid Films.* **2000**, 376 (1–2), 89–98.

(19) Kobayashi, H.; Kogetsu, Y.; Ikezumi, K.; Nakato, Y. *J. Electroanal. Chem.* **1994**, 71 (1–2), 53–58.