

Conductivities of Polysilanes

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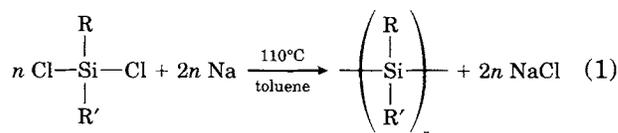
SYNOPSIS

Measurements of the electrical conductivities of three types of polysilanes were carried out over a range of dc fields and temperatures. These polymers are varied in substituents and structures with formulas of $[(C_6H_5SiCH_3)_n]$, $[(C_6H_5SiCH_3)_{70}(CH_3SiH)_{30}]_n$, and $[(C_6H_5SiCH_3)_{50}(C_6H_5SiH)_{30}(CH_3Si)_{20}]_n$. Undoped polysilanes behaved as insulators since their conductivities were observed in the range of 10^{-10} to 10^{-13} S cm^{-1} , while SbF_5 -doped polysilanes of all kinds behaved as semiconductors with conductivities in the range of 10^{-2} to 10^{-4} S cm^{-1} . No significant difference in conductivities was observed among three SbF_5 -doped polysilanes although these polymers are very different in chemical properties. These experimental results suggest that electrical conductivities of polysilanes are associated with the Si—Si main-chain backbone rather than with the side groups. It is evident that the dopant is able to diffuse throughout the bulk of the polymer and the conductivity of the doped polymer is a function of the dopant concentration from the result of *in situ* monitoring of the resistance of the silane homopolymer during SbF_5 doping at room temperature. The conductivities of polysilanes appeared to be temperature-dependent. The activation energy for the conduction of SbF_5 -doped silane copolymer was found to change at its glass transition temperature. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polysilanes (or polysilylenes) have backbones that consist entirely of Si atoms. These silicon-based polymers are chemically different from polysiloxanes (silicones), which contain both silicon and oxygen atoms alternating in the polymer chain or their carbon-based analogs, the polyalkylenes. The long chains of catenated Si atoms in the polymer backbone of polysilanes are photochemically active and display a significant degree of σ -electron delocalization.¹

Polysilanes are usually prepared using Wurtz-type reductive condensation of alkyl- or aryl-substituted dichlorosilanes with sodium agitated magnetically, mechanically, or ultrasonically²:



where R or R' is H, alkyl, or aryl group. Other synthetic routes³ have also been studied recently and include anionic ring-opening polymerization, catalytic dehydrocoupling polymerization, dehydrogenative polymerization of silanes by sigma-bond metathesis, and anionic polymerization of masked disilanes to high molecular weight polysilane of highly ordered structures.

The polymerization is highly exothermic and occurs heterogeneously on the surface² of sodium metal through a complex and largely unknown mechanism. Suitable precautions are essential for a controlled reaction. All monomers must be of high purity and the entire system should be completely dry. Oxygen should be excluded from the polymerization system

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since Si—O bonds may form when oxygen is present during the reaction. With a slight excess of sodium metal, nearly all the Si—Cl bonds in the monomers are eventually destroyed. Polysilanes with higher molecular weights, often above 100,000, are produced by the inverse addition of sodium metal dispersion to a refluxing toluene solution of highly purified substituted dichlorosilanes. Normal addition of the substituted dichlorosilane monomers to a refluxing solution containing sodium metal dispersion gives higher yields of lower molecular weight polymers.

Hydropolysilanes, a class of monosubstituted polysilanes, contain an unsubstituted hydrogen. This class of polymers possesses quite different properties from those observed in disubstituted polysilanes. For example, hydropolysilanes can be readily crosslinked by either heat or irradiation in the presence of oxygen. All these reaction characteristics of hydropolysilanes are attributed to the high reactivity of the silicon-hydride (Si—H) bond.⁴

Polysilynes, a class of amorphous silicon skeletal network materials possessing the simple stoichiometry $[\text{RSi}]_n$, were first synthesized by Bianconi and Weidman⁵ in 1988 from substituted trichlorosilane monomers. Chemical and spectroscopic analyses indicated that these materials are constructed almost entirely of sp^3 -hybridized monoorganosilyne moieties assembled into rigid and irregular networks of Si—Si σ -bonds. Polysilynes exhibit photoreactivity markedly different from that of linear polysilanes. On exposure to UV light and oxygen, polysilynes undergo a bleaching process involving the cleavage of Si—Si bonds and the formation of glasslike siloxane networks.⁵

Polysilanes possess a number of interesting chemical and electronic properties that have led to potential applications as photoresists in microlithography,⁶ nonlinear optical materials,⁷ polymerization initiators,⁸ photoconductors,⁹ semiconductors,¹⁰ and β -SiC precursors.¹¹ This article focuses on the semiconductor application.

Polysilanes are normally insulators, but an addition of strong electron acceptors, such as AsF_5 and SbF_5 , can alter the electronic properties to form semiconducting materials.^{1,10} Thus, conductivity of $[(\text{CH}_3)_2\text{Si}]_n$ in the presence of AsF_5 vapor at 700 Torr is increased from $< 1 \times 10^{-12}$ to 7×10^{-3} S cm^{-1} , and the conductivity of $\{[(\text{CH}_3)_2\text{Si}]_{0.5}[(\text{C}_6\text{H}_5)\text{SiCH}_3]_{1.0}\}_n$ in the presence of the same electron acceptor vapor at 100 Torr is increased to 5×10^{-5} S cm^{-1} . This behavior is similar to that of some organic polymers, such as polyacetylenes, which contain conjugated double bonds. However, the mechanism

of conductivity of polysilanes must be different from that of polyacetylene because there are only Si—Si single bonds in the polysilane's framework. It has been suggested that oxidation, after doping with an electron acceptor, produces a cation radical, which acts as a mobile hole, allowing the charge to move along the polymer chain.

Although semiconducting properties of disubstituted polysilanes have been studied¹⁰ and conductivities have been markedly increased by doping with strong electron acceptors such as AsF_5 , conducting mechanisms have not been clear and, thus, the results of disubstituted polysilanes cannot be certainly applied to the monosubstituted polysilanes, or hydropolysilanes, and polysilynes. In this article, we present an evaluation of conductivities of three types of polysilanes, namely, the disubstituted polysilane, the monosubstituted polysilane, and the polysilyne. The highly reactive Si—H group in the monosubstituted polysilane and the branched structure in the polysilyne are compared in terms of their effects on the conductivities.

EXPERIMENTAL

A disubstituted silane homopolymer $[\text{C}_6\text{H}_5\text{SiCH}_3]_n$ with a number-average molecular weight of 10,000, a disubstituted silane-monosubstituted silane copolymer $[(\text{C}_6\text{H}_5\text{SiCH}_3)_{70}(\text{CH}_3\text{SiH})_{30}]_n$ with a number-average molecular weight of 1300, and a disubstituted silane-monosubstituted silane-substituted silyne terpolymer $[(\text{C}_6\text{H}_5\text{SiCH}_3)_{50}(\text{C}_6\text{H}_5\text{SiH})_{30}(\text{CH}_3\text{Si})_{20}]_n$ with a number-average molecular weight of 1500 were used to examine conductivities. These three polymers were all prepared by the Wurtz-type reductive condensation from appropriate silane monomer(s) (supplied by Petrarch Systems) in refluxing toluene with molten sodium using the normal addition as described previously. The compositions and molecular weights of these polymers were determined by proton nuclear magnetic resonance analysis ($^1\text{H-NMR}$) and gel permeation chromatography (GPC), respectively.

$^1\text{H-NMR}$ analysis was performed on a polymer solution of 10 wt/vol % in deuterated chloroform. The spectra were recorded on a Bruker WP-270SY spectrometer using tetramethylsilane as a reference.

GPC traces were carried out in chloroform by a Waters pump, Model 610, and a series of Ultrastyrigel columns with pore sizes of 10^4 , 10^3 , 500, and 100 Å. A Hitachi multichannel photodiode array, Model L-3000, was used as the detector. A software system, Lab Calc, available from Galactic Industries

Corp., was used to do the necessary calculations on all GPC traces. FTIR analyses of cast thin films on KBr crystal were performed on a MATTSON Galaxy Series Model 2020 FTIR spectrophotometer.

A sketch of the sample configuration for conductivity measurements is shown in Figure 1. Samples for conductivity measurements were prepared by drop casting the polymers using a 2 wt/vol % toluene solution onto gold films (as electrodes) that had been vacuum-deposited onto quartz substrates under vacuum ($<10^{-5}$ Torr) using an Edwards Vacuum Coating Unit, Model E306A. Four electric wires, each 0.15 mm in diameter, were then attached to the gold electrodes using indium and the resulting sample was subsequently treated with dopants. Samples without the polymers were also prepared as controls.

The samples prepared as above were exposed to SbF_5 vapor in a chamber that was located in an Ar-blanketed dry bag. The chamber, equipped with a thermometer and gas outlet and connected to four wires, was then removed from the dry bag and evacuated by a vacuum pump and controlled at 5–10 Torr throughout the process. The conductivities of the doped samples were then measured without even opening the chamber.

The setup for conductivity measurements is shown in Figure 2. A dc voltage (V) between 0 and 10 V was applied and measured by an electrometer between two contacts across the polymer. The current (I), through the other two contacts, was measured by a picoammeter. The current measurements were taken 20 min after each voltage increment. All measurements were repeated a minimum of three times and were very reproducible using this experimental apparatus.

RESULTS AND DISCUSSION

Three types of polysilanes were used in this study including a homopolymer, a copolymer, and a terpolymer with the formulas $[\text{C}_6\text{H}_5\text{SiCH}_3]_n$, $[(\text{C}_6\text{H}_5\text{SiCH}_3)_{70}(\text{CH}_3\text{SiH})_{30}]_n$, and $[(\text{C}_6\text{H}_5\text{SiCH}_3)_{50}(\text{C}_6\text{H}_5\text{SiH})_{30}(\text{CH}_3\text{Si})_{20}]_n$, respectively. Polymer films of about 1 μm in thickness were prepared by

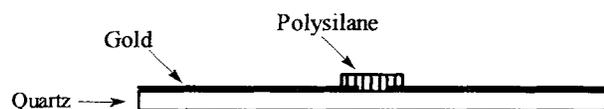


Figure 1 A sketch of the sample configuration for conductivity measurements.

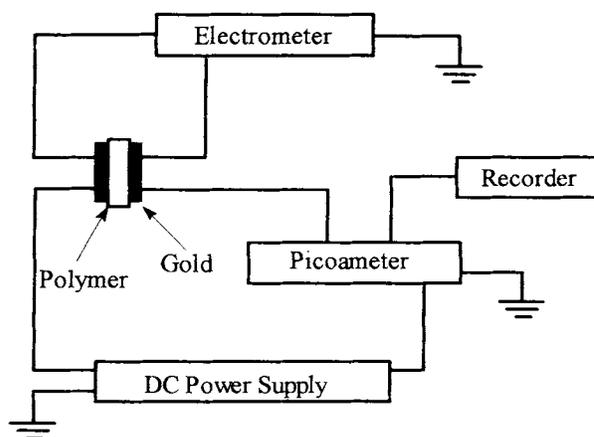


Figure 2 The schematic setup for conductivity measurements.

drop casting. The polymer films were light yellowish and transparent before doping and dark blue in color after doping with SbF_5 . The dark blue color was observed throughout the conductivity measurement but disappeared as soon as the chamber was opened and the films were exposed to air.

Conductivities, σ ($\Omega^{-1} \text{cm}^{-1}$ or S cm^{-1}), were calculated using

$$\sigma = L/(RA) \quad (2)$$

where L is the thickness (0.03 cm); R , the resistance (Ω); and A , the cross-sectional area ($5 \times 10^{-6} \text{cm}^2$). Values of R were obtained from the slopes, i.e., $\Delta V/\Delta I$, of the linear portion of I - V curves. Conductivity measurements on all films, both doped and undoped, were carried out for voltages up to 10 dc V. Since SbF_5 is a strong electron acceptor, it is very reactive to the moisture in the air; therefore, control experiments are essential to assure that conductivities are due to the polymers rather than to SbF_5 itself or its reaction product with moisture. The conductivity data were accepted only when the conductivities of the doped polymers were at least four orders of magnitude higher than those of control samples.

Undoped polysilanes were shown to be insulators since their conductivities were observed in the range of 10^{-10} to $10^{-13} \text{S cm}^{-1}$. All SbF_5 -doped polysilanes were shown to be semiconductors since their conductivities were found in the range of 10^{-2} to 10^{-4}S cm^{-1} . Conductivities at room temperature of three types of polysilanes studied are compared in Figure 3. The conductivities of the three polysilanes were all in the range of 10^{-2} to 10^{-4}S cm^{-1} . There was no significant difference in conductivity among three types of polysilanes. The terpolymer had the highest

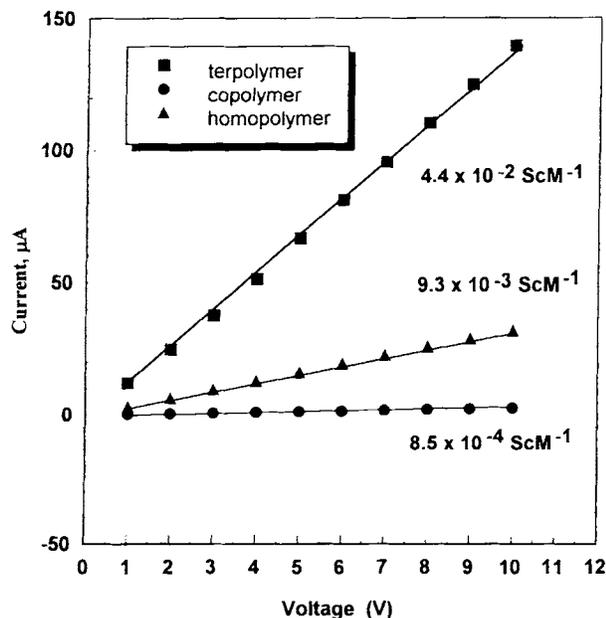


Figure 3 Conductivities at room temperature of three types of polysilanes.

conductivity, being about one and two orders of magnitude higher than the homopolymer and the copolymer, respectively. It is still unclear what causes the differences. West and co-workers¹⁰ found that a crosslinked polysilane provides a higher conductivity than does an uncrosslinked one. Thus, a branched structure in the terpolymer may explain the reason why the terpolymer had a higher conductivity than that of the homopolymer and the copolymer. The conductivity of the homopolymer was higher than that of the copolymer. The higher phenyl group content in the homopolymer than in the copolymer may be the explanation since the phenyl groups may provide the resonance effect and/or form complexes with SbF_5 to lower the ionization potential and thus facilitate the formation of cation radicals, which are believed to be the carriers that make polysilanes conductive after SbF_5 doping. The formed complexes may be evidenced by the dark blue in color of the doped silane polymers. Si—H groups have not been found to have any significant effect on the conductivity of the SbF_5 -doped copolymer, or hypopolysilane, although the FTIR spectra (not shown) of the copolymer shows a depletion of the Si—H stretching band at 2079 cm^{-1} after doping with SbF_5 .

In situ monitoring of the resistance during SbF_5 doping has been done on the homopolymer at room temperature. Results are shown in Figure 4. The resistance of the polymer film is very high in the

beginning, decreases rapidly after 30 min, and then levels off at about 100 min of doping. This behavior suggests that the dopant is able to diffuse throughout the bulk of the polymer and the conductivity of the doped polymer is a function of the dopant concentration.

The conductivity of polysilanes appears to be temperature-dependent as shown in Figure 5 for the terpolymer. Figure 6 shows Arrhenius plots of $\log(I)$ as a function of $1/T$ for three polymers at 5 V. The activation energies were calculated using the Arrhenius expression shown below:

$$\ln(I) = \ln(A_0) - E_a/(kT) \quad (3)$$

where I is the current (μA); A_0 , a constant; E_a , the activation energy (J); k , the Boltzmann constant ($1.381 \times 10^{-23}\text{ J K}^{-1}$); and T , the absolute temperature (K). Activation energies (E_a) are determined from the slope of the Arrhenius plots. The Arrhenius plots (Fig. 6) of $\log(I)$ as a function of $1/T$ at constant electric field were linear in the temperature range of measurements for the terpolymer and the homopolymer with activation energies being 0.21 and 0.38 eV, respectively. However, there is a turning point in the Arrhenius plot of the copolymer at 49°C that is close to its glass transition temperature (T_g) of 51°C .¹² A lower activation energy of 0.27 eV was observed for the copolymer for temperatures over its T_g , while 0.8 eV was obtained for temperatures under its T_g . The glass transition temperatures for

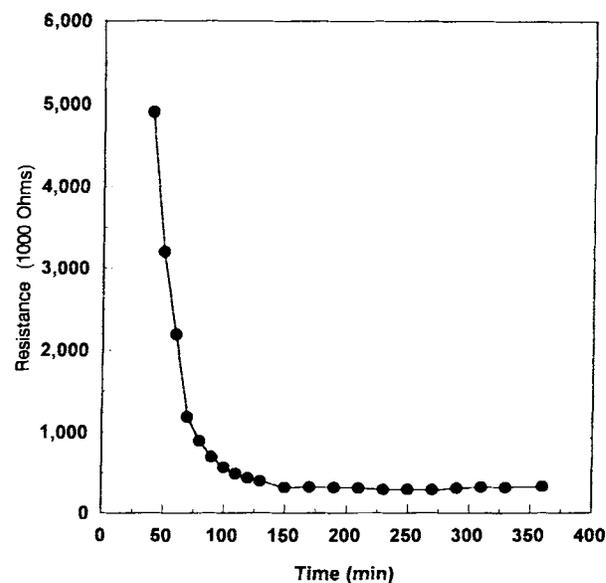


Figure 4 The resistance at room temperature of the silane homopolymer as a function of doping time using SbF_5 as the dopant.

the homopolymer and the terpolymer are 117 and 89°C,¹² respectively.

CONCLUSIONS

Electrical-conducting properties of three types of polysilanes with varied substituents and structures, their formulas being $[\text{C}_6\text{H}_5\text{SiCH}_3]_n$, $[(\text{C}_6\text{H}_5\text{SiCH}_3)_{70}(\text{CH}_3\text{SiH})_{30}]_n$, and $[(\text{C}_6\text{H}_5\text{SiCH}_3)_{50}(\text{C}_6\text{H}_5\text{SiH})_{30}(\text{CH}_3\text{Si})_{20}]_n$, were studied. Undoped polysilanes behave as insulators since their conductivities were observed in the range of 10^{-10} to 10^{-13} S cm^{-1} , while SbF_5 -doped polysilanes of all kinds behave as semiconductors with conductivities in the range of 10^{-2} to 10^{-4} S cm^{-1} . No significant difference in conductivities was observed among three polysilanes after SbF_5 doping although these polymers are quite different in chemical properties due to the high reactivity of the Si—H group in the copolymer and the branched structure in the terpolymer. This observation suggests that the conductivities of polysilanes may depend on the conducting carriers (cation radicals) transporting dominantly through the polymer backbone rather than on the substituents. Although their effects were not significant, the branched structure and phenyl substituent were found to be helpful in pro-

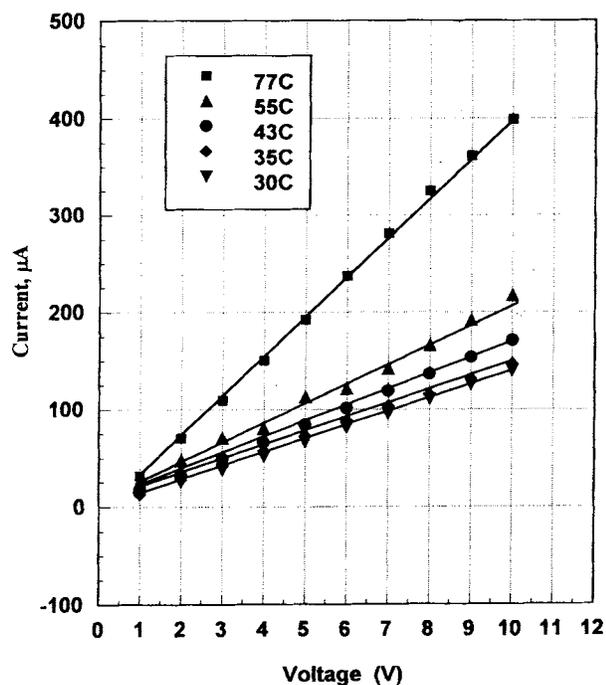


Figure 5 The I - V curves of the terpolymer after doping with SbF_5 as a function of temperatures.

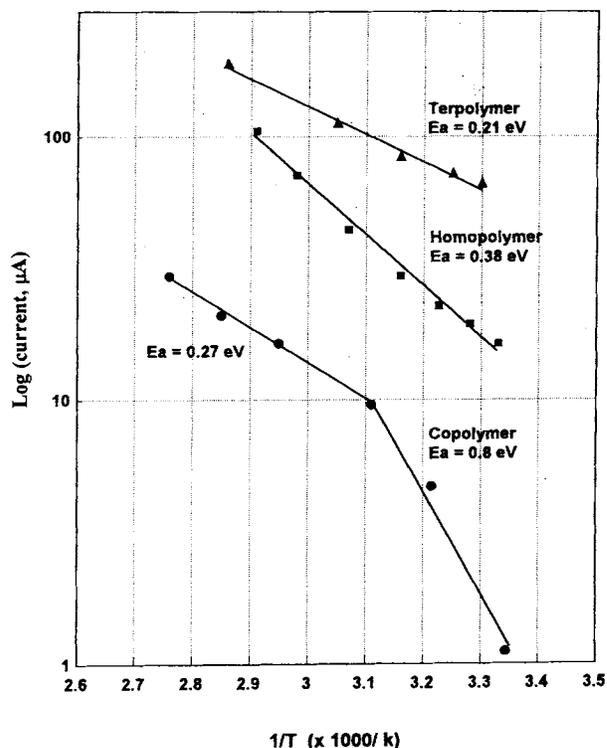


Figure 6 The currents as a function of temperatures at 5 V of electric field for the silane homopolymer, copolymer, and terpolymer.

moting conductivities of polysilanes. Based on the result from *in situ* monitoring of the resistance of the homopolymer during SbF_5 doping at room temperature, it is suggested that the dopant is able to diffuse throughout the bulk of the polymer and the conductivity of the doped polymer is a function of the dopant concentration. The conductivities of polysilanes appeared to be temperature-dependent. The activation energy for the conduction of SbF_5 -doped silane copolymer was found to change at its T_g .

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