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PII: S0032-3861(97)00054-2

Polymer Vol. 38 No. 20, pp. 5015–5021, 1997
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0032-3861/97/$17.00 + 0.00

Photoreaction of alkoxypolysilanes

K. Kabeta*, S. Sugi, S. Wakamatsu and T. Imai*
New Materials Laboratory, Toshiba Silicone Co. Ltd, 133 Nishishinmachi, Ohta, 373, Japan
(Received 21 June 1996; revised 16 December 1996)

The photoreaction of network ethoxypolysilanes ($(MeSi)_n[Me(EtO)Si]_m$) using low pressure mercury lamps was investigated in the presence and in the absence of oxygen, and was compared with that of poly(hexylsilyne) and poly(dihexylsilylene). The photoreaction of the ethoxypolysilanes in the presence of oxygen led to their photooxidation, and resulted in a decreased molecular weight and the disappearance of ultraviolet absorption over 300 nm. The molecular weight of the ethoxypolysilanes was more slowly reduced than that of poly(hexylsilyne). On the other hand, photolysis of the ethoxypolysilanes under an inert atmosphere caused an increase in molecular weight, though similar photolysis of the alkylpolysilanes showed a molecular weight decrease. These results could be explained by the influence of the ethoxysilyl groups in the polysilanes. The decomposition of polymer chains would be depressed by the reaction of the alkoxysilyl groups with silanols produced from photooxidation and the insertion reaction of silylenes into Si–OEt bonds. © 1997 Elsevier Science Ltd.

(Keywords: alkoxypolysilane; photoreaction; photooxidation)

INTRODUCTION

Polysilanes have recently attracted considerable attention, due to their unusual electronic and photophysical properties[1,2], as well as their potential applications as photoresists[3], photoconductors[4], waveguides[5], and nonlinear optical materials[6]. For some of these applications, photochemical stability of the materials was considered to be one of the most important requirements, because polysilanes are known to be photoreactive. On the contrary, it was desirable that polysilanes used as photoresists have the highest possible photo-sensitivity[7].

We have launched an investigation into polysilanes, for use as a material for electrically conducting circuits. Polysilanes are thought to be among the best candidates for this application, because polysilanes are known to be electrically conductive upon doping[8], and polysiloxane, which is produced by photochemical conversion of the pristine polysilane, is basically an insulating material. The combination of the photoreactivity of the polysilane and the properties of these two materials would allow electrically conducting circuits to be directly fabricated in the polysilane thin films using standard photolithographic techniques.

We have already studied the correlation between the polysilane backbone structure and photooxidation tendency, in order to find a suitable structure for the above application[9]. Polysilanes containing a greater number of silyne units, that is, highly branched polysilanes, required a greater dose of ultraviolet (u.v.) exposure for the completion of the photooxidation. The degradation of the networked and branched polysilanes was slower, and less than that of linear polymers during the reactions. There are some other reports about the influence of the backbone structures on the photochemical behaviour under an inert atmosphere[10,11], and a network polysilyne was reported to be more photostable than a linear polysilylene[12]. For the photooxidation reaction, the network polysilyne was found to be difficult to degrade, whereas the linear polysilylene was easily degraded and generated smaller cyclic oligomers[12].

We have also investigated a preparation method for network methylethoxypolysilanes by the disproportionation reaction of alkoxydisilanes[13–16]. This preparation method is considered to be an economical and convenient industrial process for polysilane materials, because this procedure possesses some advantages over other methods such as the Wurtz-type coupling reaction; the reaction conditions are mild, the procedure is simple and safe, many kinds of substituents onto silicon atoms are easily introduced, and the starting materials are readily available from methylchlorodisilanes, which are the by-products of the industrially operated direct synthesis of methylchlorosilanes.

We then started to attempt to use these network ethoxypolysilanes as a material for electrically conducting circuits. First of all it was important to examine the nature of the photooxidation reaction of these polysilanes in order to determine the suitability for this application. To the best of our knowledge, however, there are no reported studies of the photoreaction of polysilane polymers containing a certain amount of alkoxy groups. Therefore, we have studied the photoreaction of the alkoxypolysilanes. In this paper, we report on the results of a photoreaction of the alkoxypolysilanes mainly obtained by the disproportionation reaction, both in the presence and in the absence of oxygen, in comparison with the photoreaction of alkylpolysilanes.

EXPERIMENTAL

Materials

1,1,2,2,-Tetraethoxy-1,2-dimethyldisilane was prepared

* To whom correspondence should be addressed

by the reaction of 1,1,2,2,-tetrachloro-1,2-dimethyldisilane with ethanol in the presence of pyridine. 1,1,2,2-Tetrachloro-1,2-dimethyldisilane was obtained from selective chlorination of a so-called 'disilane residue' from the direct synthesis for commercial silicone production using acetyl chloride and anhydrous aluminium chloride[17]. The disilane residue was normally a mixture of 1,1,2,2-tetrachloro-1,2-dimethyldisilane (*ca* 65%) and 1,1,2-trichloro-1,2,2-trimethyldisilane (*ca* 35%). Methyllithium (1.0 M or 1.1 M in diethyl ether), butyllithium (1.6 M in hexanes), 2,5-dibromothiophene, triethylsilane, trimethylethoxysilane, phenylsilane, hexylsilane and dry THF were commercially available. Poly(hexylsilyne)[18] (**2**, $M_w = 26000$ ($M_w/M_n = 4.2$)) and poly(dihexylsilylene)[19] (**3**, $M_w = 15800$ ($M_w/M_n = 1.8$)) were prepared according to the literature procedures. These polysilanes were purified by reprecipitation using methanol/toluene mixed solvents. Hexane or cyclohexane, which was dehydrated by sodium, was used as the solvent for the photooxidation reactions. Oxygen gas (purity: over 99.95%) was dehydrated by passage through a calcium chloride drying tube just before introduction into the reaction mixture.

Measurements

Ultraviolet–visible (u.v.–vis) absorption spectra were measured on a Hitachi U-3500 spectrometer. Infra-red (i.r.) spectra were measured on a Shimadzu IR-47 i.r. spectrometer. ^{1}H and ^{29}Si nuclear magnetic resonance (n.m.r.) spectra were measured using a Bruker ARX-400 spectrometer with a tetramethylsilane external standard. The molecular weight and polydispersity were determined for the photoreaction in the presence of oxygen by size exclusion chromatography (s.e.c.) using a JASCO 801-SC system controller, a JASCO 880-PU HPLC pump, a JASCO 870 u.v. detector at 254 nm and a JASCO 830 refractive index detector equipped with two Shodex GPC L-806L (8 × 300 mm) columns. Chloroform was used as the eluent, and the calibration was performed using monodispersed polystyrene standards. For the reaction under an inert atmosphere, the molecular weight was measured using a Shodex GPC System-11 gel permeation chromatograph equipped with two Shodex GPC L-804L (8 mm × 300 mm) columns. Tetrahydrofuran was used as the eluent and calibration was performed using monodispersed polystyrene standards. Gas chromatography (g.c.)–i.r.–mass spectrometric (m.s.) analysis was performed on a Hewlett-Packard 5890 II g.c., a 5965B i.r. detector and a 5972 mass selective detector equipped with a J & W Scientific DB-1 column (30 m × 0.32 mm × 0.25 μm). G.c.s were measured on a Shimadzu GC-14A g.c. using a flame ionization detector (FID) and an HP-5 M.S. column (30 m × 0.25 mm × 0.25 μm).

Preparation of methylethoxypolysilanes **1a**, **1c** *and* **1d**

As a representative example, the preparation of **1a** is described. In a 50-ml two-necked, round-bottomed flask equipped with a reflux condenser, a magnetic stirrer bar and a rubber septum, were placed 2.0 g (7.5 mmol) of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane and 5 ml of dry tetrahydrofuran. To the mixture, 0.15 ml (0.17 mmol) of 1.1 M methyllithium in diethyl ether was added by a syringe at room temperature under an argon atmosphere. The reaction mixture was then heated to 100°C for 10 h. The reaction mixture turned yellow on heating. After the complete disappearance of the disilane peak in the g.c. chromatogram, the insoluble lithium salt was filtered off and the filtrate was added to 100 ml of absolute methanol. Subsequent filtration of precipitated solid and drying *in vacuo* gave 170 mg of white powder. The u.v. absorption tailed down to 400 nm and indicated a network polysilane framework[12]. ^{1}H n.m.r. ($CDCl_3$, δ) 0.4 (*br. s*, 54 H, $SiCH_3$), 1.2 (*t*, $J = 7$ Hz, 14 H, Si–O–C–CH_3), 3.7 (*q*, $J = 7$ Hz, 9 H, Si–O–CH_2); i.r. (KBr) 2960, 2940, 1400, 1260, 1065, 1010, 760 cm^{-1}; $M_w = 11\,000$ ($M_w/M_n = 3.5$).

1c. To a solution of 5.0 g (19 mmol) of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane and 5 ml of dry THF, 0.26 ml (0.29 mmol) of 1.1 M methyllithium in diethyl ether was added. After the reaction mixture was stirred at 100°C for 5 h, 650 mg of **1c** was obtained as a white powder by the same work-up procedure as that described above. The u.v. absorption tailed down to 380 nm. ^{1}H n.m.r. ($CDCl_3$, δ) 0.3 (*br. s*, 55 H, $SiCH_3$), 1.3 (*t*, $J = 7$ Hz, 12 H, Si–O–C–CH_3), 3.7 (*q*, $J = 7$ Hz, 8 H, Si–O–CH_2); i.r. (KBr) 2950, 2910, 1450, 1260, 1060, 1010, 740 cm^{-1}; $M_w = 2800$ ($M_w/M_n = 1.8$).

1d. To a solution of 5.0 g (19 mmol) of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane and 5 ml of dry THF, 0.65 ml (0.72 mmol) of 1.1 M methyllithium in diethyl ether was added. After the reaction mixture was stirred at 100°C for 20 h, 500 mg of **1d** was obtained as a white powder by the same work-up procedure as described above. The u.v. absorption tailed down to 400 nm. ^{1}H n.m.r. ($CDCl_3$, δ) 0.3 (*br. s*, 57 H, $SiCH_3$), 1.3 (*t*, $J = 7$ Hz, 9 H, Si–O–C–CH_3), 3.7 (*q*, $J = 7$ Hz, 6 H, Si–O–CH_2); i.r. (KBr) 2950, 2910, 1450, 1235, 1060, 1010, 740 cm^{-1}; $M_w = 23800$ ($M_w/M_n = 6.3$).

Preparation of methylethoxypolysilane **1b**

In a 50-ml two-necked, round-bottomed flask equipped with a reflux condenser, a magnetic stirrer bar and a rubber septum, was placed 10 mg (0.15 mmol) of sodium ethoxide. To the flask, 2.0 g (7.5 mmol) of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane was added by a syringe at room temperature under an argon atmosphere. The reaction mixture was then heated to 120°C for 18 h. The reaction mixture turned yellow on heating. After the complete disappearance of the disilane peak in the g.c. chromatogram, insoluble sodium ethoxide was filtered off and the filtrate was added to 100 ml of absolute methanol. Subsequent filtration of precipitated solid and drying *in vacuo* gave 190 mg of white powder. The u.v. absorption tailed down to 400 nm. ^{1}H n.m.r. ($CDCl_3$, δ) 0.4 (*br. s*, 30 H, $SiCH_3$), 1.2 (*t*, $J = 7$ Hz, 6 H, Si–O–C–CH_3), 3.7 (*q*, $J = 7$ Hz, 4 H, Si–O–CH_2); i.r. (KBr) 2960, 2930, 1400, 1260, 1065, 1010, 760 cm^{-1}; $M_w = 5700$ ($M_w/M_n = 1.9$).

Preparation of methylethoxy(thiophene-2,5-diyl) polysilane **1e**

To a solution of 230 mg (0.95 mmol) of 2,5-dibromothiophene and 5 ml of dry THF, 0.75 ml (1.9 mmol) of 1.6 M butyllithium in hexanes was added by a syringe at 0°C under an argon atmosphere. The reaction mixture was stirred at room temperature for 3 h, and a solution of 2,5-dilithiothiophene was obtained. To the reaction mixture, 5.0 g (19 mmol) of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane was added by a syringe at room temperature. The reaction mixture was then heated to 100°C for 20 h. After the complete disappearance of the

disilane peak in the g.c. chromatogram, the insoluble lithium salt was filtered off and the filtrate was added to 180 ml of absolute methanol. Subsequent filtration of the precipitated solid and drying *in vacuo* gave 600 mg of white powder. The u.v. absorption tailed down to 400 nm. ^{1}H n.m.r. ($CDCl_3$, δ) 0.5 (*br. s*, 175 H, $SiCH_3$), 1.3 (*t*, $J = 7$ Hz, 26 H, Si–O–C–CH_3), 3.7 (*q*, $J = 7$ Hz, 18 H, Si–O–CH_2), 6.8–7.5 (*m*, 4 H, C_4H_2S); i.r. (KBr) 3045, 2980, 2950, 1450, 1230, 1050, 1010, 740 cm^{-1}; $M_w = 5200$ ($M_w/M_n = 1.9$).

Preparation of poly(phenylethoxysilylene) **4**[20]

Poly(phenylhydrosilylene) was synthesized from phenylsilane by a reported method using a catalyst generated *in situ* from the reaction of dichlorozirconocene with methyllithium[21]. ^{1}H n.m.r. ($CDCl_3$, δ) 4.1–5.8 (*m*, 1 H, SiH), 6.5–8.1 (*m*, 5 H, Ph H); i.r. (neat) 3050, 2100, 1510, 1090, 700 cm^{-1}; $M_w = 1900$ ($M_w/M_n = 1.5$).

Poly(phenylethoxysilylene) **4**, was then prepared according to the literature procedure described below[20]. To 5.0 g of poly(phenylhydrosilylene), 50 ml of carbon tetrachloride was slowly added using a syringe at 0°C under an argon atmosphere, after which the reaction mixture was refluxed for 8 h. Monitoring of the reaction by i.r. (Si–H absorption band around 2100 cm^{-1}) indicated that the chlorination reaction no longer proceeded after 8 h. Removal of volatile materials under reduced pressure gave the poly(phenylchlorosilylene). ^{1}H n.m.r. ($CDCl_3$, δ) 4.0–5.8 (*m*, trace amount, SiH), 6.0–8.2 (*m*, 5 H, Ph H); i.r. (neat) 3050, 2100, 1040, 670 cm^{-1}.

To a solution of the entire amount of poly(phenylchlorosilylene) and 50 ml of dry toluene, a mixture of 5.0 ml of triethylamine and 5.0 ml of absolute ethanol was added. The reaction mixture was allowed to react for 8 h at room temperature. After volatile materials were removed under reduced pressure, 50 ml of hexane was added. A precipitated solid was filtered off, the concentration of the filtrate under reduced pressure yielded 2.3 g of yellow oil **4**. ^{1}H n.m.r. ($CDCl_3$, δ) 0.3–1.7 (*m*, 3 H, O–C–CH_3), 2.9–4.2 (*m*, 2 H, O–CH_2–C), 6.1–8.1 (*m*, 7 H, Ph H); i.r. (neat) 3050, 2100, 1430, 1100, 700 cm^{-1}; $M_w = 2000$ ($M_w/M_n = 1.2$). N.m.r. and i.r. data suggested that the Si–H and Si–Cl groups remained in the product.

Preparation of poly(hexylethoxysilylene) **5**

Poly(hexylethoxysilylene) **5**, was prepared by the same procedure for **4** except for the usage of hexylsilane.

poly(hexylhydrosilylene). ^{1}H n.m.r. ($CDCl_3$, δ) 0.9 (*br. s*, 2 H, $SiCH_2$), 1.4 (*br. s*, 3 H, CH_3), 1.7 (*br. s*, 8 H, Si–C–$(CH_2)_4$–C), 3.8–4.5 (*m*, 1 H, SiH); i.r. (neat) 2960, 2910, 2840, 2080, 1460, 795 cm^{-1}; $M_w = 1400$ ($M_w/M_n = 1.1$).

5. 15% yield from poly(hexylhydrosilylene). ^{1}H n.m.r. ($CDCl_3$, δ) 0.9 (*br. s*, 2 H, $SiCH_2$), 1.2 (*br. s*, 1.8 H, O–C–CH_3), 1.3 (*br. s*, 3 H, C–C–CH_3), 1.5 (*br. s*, 8 H, Si–C–$(CH_2)_4$–C), 3.5–3.9 (*m*, 1.2 H, O–CH_2–C); i.r. (neat) 2960, 2915, 2835, 2105, 1470, 1035 cm^{-1}; $M_w = 1900$ ($M_w/M_n = 1.2$). N.m.r. and i.r. data suggested that the Si–H and Si–Cl groups remained in the product.

Photoreaction in the presence of oxygen

The photooxidation of the polysilanes (100 mg) in dry hexane solution (200 ml) was carried out using a merry-go-round type photolysis apparatus and a low pressure mercury lamp (cold cathode type, Riko-Kagaku Sangyo Co., Ltd, UVL-32LB, 32 W) with a stream of dry oxygen gas (1.7 ml s^{-1}). The progress of the photooxidation reactions was monitored by u.v.-vis absorption spectroscopy and s.e.c. The experiments were carried out at room temperature.

Photoreaction in the absence of oxygen

The photoreaction of the polysilanes in the absence of oxygen was carried out as follows. In a quartz photolysis tube equipped with a three-way stopcock and a magnetic stirrer bar were placed 25 mg of the polysilanes and 10 ml of dry hexane. For the photolysis of poly(phenylethoxysilylene) (**4**), dry cyclohexane was used instead of hexane because of the low solubility of the polysilane. After three freeze–pump–thaw degassing cycles, the solution was placed at the centre of seven low pressure mercury lamps (cold cathode type, Eye Graphics, QGL30W-21, 30 W), and stirred and irradiated for 5–60 min. The experiments were carried out at room temperature.

Photoreaction in the presence of trimethylethoxysilane or triethylsilane

The photoreactions of **1e** (25 mg, 0.61 mmol per Si–Si unit) in 5 ml of dry hexane were separately carried out in the presence of trimethylethoxysilane (3.8 g, 32 mmol) or triethylsilane (3.7 g, 32 mmol), in the same manner described for the photoreaction in the absence of oxygen.

Photooxidation reaction of a methylethoxypolysilane film

Methylethoxypolysilane film was prepared on a quartz plate using 5% tetrahydrofuran solution (w/w) by the spin-coating technique (500 rpm 10 s, 2000 rpm 20 s) followed by drying *in vacuo* (3 Torr) at 50°C for 1 h. A film thickness of 0.7 μm was measured using a stylus profilometer (Taylor–Hobson, Ltd). The film was irradiated using a low pressure mercury lamp (cold cathode type, Eye Graphics, QGL30W-21, 30W) in air at room temperature, and the reaction was monitored by u.v. spectroscopy. The integral exposure of u.v. light was measured using an ORC UV-M30 instrument with a UV-25 sensor (254 nm).

RESULTS AND DISCUSSION

Photoreaction in the presence of oxygen

Network methylethoxypolysilane (**1a**), which was used for the study of the photooxidation reaction, was prepared by a disproportionation reaction of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane initiated by the addition of a small amount of methyllithium as shown in equation (1)[15,16]. The unit ratio of the polysilane was estimated to be $(MeSi)_n[Me(EtO)Si]_m$ ($n/m = 75/25$) based on ^{1}H n.m.r. without consideration of Me_2Si units or polymer ends. Therefore, the extent of the network degree of this polysilane was considered to be between polysilyne $(RSi)_n$ and polysilylene $(RR'Si)_n$.

$$Me(EtO)_2SiSi(OEt)_2Me \xrightarrow{MeLi} (MeSi)_n[Me(EtO)Si]_m \quad (1)$$

$$(n/m = 75/25)$$

1a

According to the observation about the correlation of the photooxidation tendency with the polymer backbone structure[9], both the disappearance of u.v. absorption and

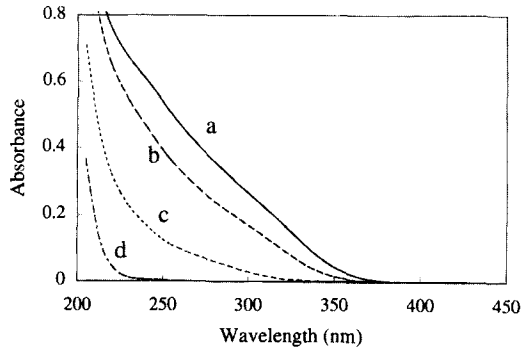

Figure 1 U.v. absorption spectra of **1a** before and after irradiation ($12.5\,mg\,l^{-1}$ in hexane): (a) before irradiation; (b) irradiation for 180 s; (c) irradiation for 600 s, (d) irradiation for 1800 s

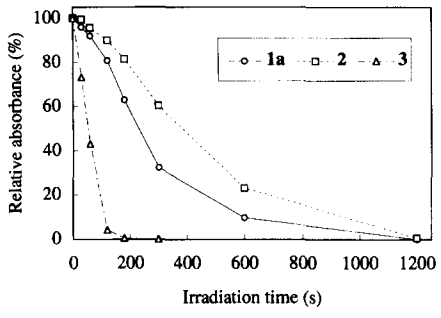

Figure 2 Variation in u.v. absorbance ratios of **1a**, **2** and **3** for the photooxidation reaction. The ratios were calculated from the absorbance at an absorption of 315 nm and based on each absorption before irradiation

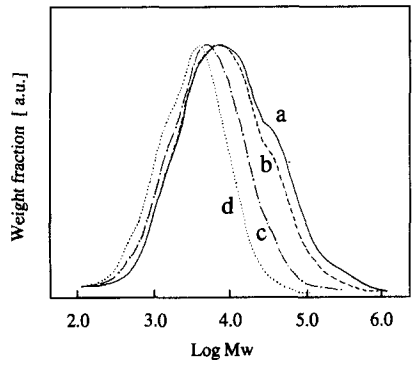

Figure 3 S.e.c. chromatograms of **1a** using refractive index and u.v. (254 nm) detectors before and after irradiation: (a) before irradiation; (b) irradiation for 180 s; (c) irradiation for 600 s; (d) irradiation for 1800 s

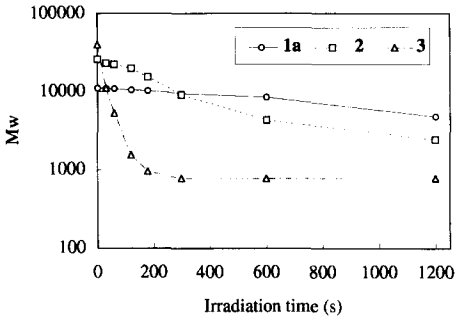

Figure 4 Variation in the weight-average molecular weights of **1a**, **2** and **3** using refractive index and u.v. (254 nm) detectors for the photooxidation reactions

the decrease in molecular weight for **1a** were anticipated to be faster than those of poly(hexylsilyne) (**2**) and slower than those of poly(dihexylsilylene) (**3**).

The photooxidation reaction of **1a** was carried out in hexane solution using a low pressure mercury lamp, and the reaction was monitored by u.v. absorption spectroscopy and s.e.c. U.v. spectra before and after the photooxidation reaction of **1a** are shown in *Figure 1*. The conversion of a Si–Si bond in the polysilane into a Si–O–Si linkage led to shortened Si–Si chains and resulted in diminishing the u.v. absorption similar to the photooxidation of other polysilanes[9]. The strong absorption bands were observed around $1100\,cm^{-1}$ (Si–O–Si) and $3450\,cm^{-1}$ (Si–OH) in the i.r. spectrum of the resulting reaction mixture, which indicated the progress of photooxidation. A small signal at $2170\,cm^{-1}$, which was ascribed to a Si–H bond, was also detected. The ^1H n.m.r. of the product obtained after removal of the volatile compounds was almost identical with that of **1a** except for the 40% reduction of the integral for the signal ($\delta = 3.7$ ppm), ascribed to ethoxy methylene using a $Si–CH_3$ signal as a criterion. We could explain this result by the reaction of silanol produced from the photolysis with a Si–OEt group in the polymer. The reaction would yield a Si–O–Si linkage and ethanol, and the ethanol was excluded during the solvent removal step from the reaction mixture.

The decrease in absorbance at a u.v. absorption of 315 nm is plotted as a function of irradiation time in *Figure 2*, along with the results of the photooxidation of **2** and **3** under the same conditions, in order to compare their relative photoreactivity to the light of low pressure mercury lamp as materials. Because **3** showed an absorption maximum at 315 nm, but **1a** and **2** did not display apparent maxima in the observed u.v. region, we chose an absorbance of 315 nm to follow the reactions. The order of the decrease in the u.v. absorption was as previously expected, that is, the order was consistent with the network degree of the polymers. Polysilyne **2** required the largest amount of exposure dose, polysilylene **3** required the smallest amount, and polysilane **1a**, which consisted of silyne and silylene units (the ratio was estimated to be 75/25), required an intermediate amount.

If we take absorption coefficients of these polymers at 254 nm into account, the discussion of the polymer properties could be more precise. Although the coefficients would change as the photooxidation reaction proceeded, because the contiguous Si–Si bonds length would be shortened by the insertion of an oxygen to the Si–Si bonds, we made an assumption that the relative change of the coefficients among the polymers were consistent. The absorption coefficients per Si–Si unit at 254 nm of **1a**, **2** and **3** were respectively determined to be 2.1×10^3, 2.3×10^3 and $1.3 \times 10^3\,l\,mol^{-1}\,cm^{-1}$. Consequently, the corrected difference in photo-reactivity of **1a** and **2** were greater than the difference displayed in *Figure 2*.

On the other hand, the order of the molecular weight change was different from what we anticipated. The s.e.c. chromatograms of **1a** before and after irradiation are illustrated in *Figure 3*, and the weight-average molecular weights of **1a**, **2** and **3** are plotted as a function of irradiation time in *Figure 4*. The molecular weight decrease of **1a** was slower than that of polysilylene **3**, as we expected; however, the decrease in the molecular weight of polysilyne **2** was faster than that of **1a**. The

order was the same, even though the absorption coefficients of initial polymers were taken into consideration. When network methylethoxypolysilane **1b** (unit ratio, $(MeSi)_n[Me(EtO)Si]_m$, $n/m = 80/20$; initial M_w, 5700 ($M_w/M_n = 1.9$); absorption coefficient at 254 nm, $2.0 \times 10^3\,l\,mol^{-1}\,cm^{-1}$) was irradiated under the same conditions, the molecular weight was only reduced to 5450 ($M_w/M_n = 2.3$) after a 10-min irradiation.

This phenomenon could be caused by the influence of the ethoxy groups in the polysilanes. Silylenes and silyl radicals are known to be formed by the photolysis of polysilanes[22]. It is reported that the irradiation by a light over 300 nm mainly produced silyl radicals, but on the other hand, irradiation by a light at 254 nm (low pressure mercury lamp) produced both silylenes and silyl radicals[23,24]. One of two probable reasons for the slow molecular weight change of **1a** is the reaction of ethoxysilyl groups in the polymer with silanols which were produced from these active species. Another reason would be the insertion reaction of the silylenes into the Si–O bonds of the ethoxysilyl groups. Such an insertion reaction of photochemically generated silylenes into dimethoxydimethylsilane was reported by Ishikawa and Kumada[25]. The insertion of thermally generated silylenes into alkoxysilanes and alkoxyoligosilanes was disclosed by Atwell and coworkers[26,27]. Fast disappearance of the u.v. absorption of **1a** indicated that the former reason would be more significant because, if the latter insertion reaction is predominant, the change in u.v. absorption could be very slow. The number of Si–Si bonds must be unchanged in the latter entire reaction system. The formation of silyl radicals and silylenes from **2**, which only has methoxy groups at the polymer ends, would mainly lead to decomposition of the polymer chain. For our patterning application, the smallest molecular weight change is preferable, whereas high sensitivity to the light could be essential for the photolithographic usage, as already mentioned. From these points of view, network methylethoxypolysilane **1a** would be more suitable for photolithographic applications than polysilyne **2**.

The photooxidation reaction of a thin film of **1a** was then carried out. It is important for a practical application that the pristine polysilane films remained as a solid after the photooxidation, because liquefaction would lead to a collapse in the film shape. For example, the poly(cyclohexylmethylsilylene) film was known to be liquefied after photooxidation[9]. The thin film was irradiated using a low pressure mercury lamp in the air, and the film was found to be still solid after the u.v. absorption over 300 nm completely disappeared.

Photoreaction in the absence of oxygen

Photoreaction of the polysilanes in the absence of oxygen was carried out in order to investigate the influence of the ethoxysilyl group of polysilanes, as already mentioned. The polysilane solutions were irradiated for 20 min using a low pressure mercury lamp under an inert atmosphere, and the molecular weight and u.v. spectra of the reaction mixtures were measured before and after the reactions. The changes in the weight-average molecular weights of polysilanes are summarized in *Table 1*. The molecular weight of network ethoxypolysilanes **1a**, **1c** and **1d** increased and polydispersity of these polysilanes became greater after the photoreaction. This phenomenon was independent of both the initial molecular weight and the initial unit ratio. The molecular weight and the polydispersity of **1e**, which contained a small amount of thiophene groups, were changed in a similar way. On the contrary, the molecular weight of alkylpolysilanes **2** and **3** decreased. As examples of linear alkoxypolysilanes, poly(phenylethoxysilylene) (**4**) and poly(hexylethoxysilylene) (**5**) were examined. Although the polysilanes contained a certain amount of Si–H and Si–Cl groups in the polymer, and these groups might affect both the reaction and the product, the molecular weight of the polysilanes increased after the photoreaction. The large molecular weight increase of **4** could partially be due to the contribution of the phenyl groups in the polymer[28].

The molecular weight distribution change of the network methylethoxypolysilane (**1c**) is illustrated in *Figure 5* along with the results of poly(hexylsilyne) (**2**) and poly(dihexylsilylene) (**3**). The u.v. absorption spectra of the polysilanes were changed by the photoreaction as shown in *Figure 6*. The amount of the irradiation dose was enough to stop the u.v. absorption above 300 nm of the linear polysilane **3**. However, a slight decrease in u.v. absorption was observed for the photoreaction of **1c** and **2**, which indicated the presence of Si–Si chains. The photoreaction shifted the molecular weight distribution of the network methylethoxypolysilane **1c** to the higher molecular weight side, and the distribution became

Table 1 Molecular weight change of polysilanes before and after photoreaction using low pressure mercury lamps under an inert atmosphere

Run	Polysilane		ϵ^a ($\times 10^{-3}$)	M_w (M_w/M_n)[b] Before exposure	After exposure
1	$(MeSi)_n[Me(EtO)Si]_m$ ($n/m = 75/25$)[c]	**1a**	2.1	11 000 (3.5)	47 000 (8.5)
2	$(MeSi)_n[Me(EtO)Si]_m$ ($n/m = 78/22$)[c]	**1c**	1.3	2800 (1.8)	15 400 (3.0)
3	$(MeSi)_n[Me(EtO)Si]_m$ ($n/m = 84/16$)[c]	**1d**	1.6	23 800 (6.3)	120 000 (18)
4	$(MeSi)_n[Me(EtO)Si]_m(C_5H_2S)_p$ ($n/m/p = 84/13/3$)[c]	**1e**	1.2	5200 (1.9)	41 000 (12)
5	$(HexSi)_n$	**2**	4.6	26 000 (4.2)	18 900 (3.0)
6	$(Hex_2Si)_n$	**3**	1.9	15 800 (1.8)	1200 (1.4)
7	$[Ph(EtO)Si]_n$[d]	**4**	2.3	2000 (1.1)	9800 (4.9)
8	$[Hex(EtO)Si]_n$[d]	**5**	1.3	1900 (1.2)	2000 (1.2)

[a] Absorption coefficient of initial polymer at 254 nm per Si–Si unit in hexane (runs 1–6, 8) or in cyclohexane (run 7)
[b] Measured by s.e.c. using a refractive index detector (vs polystyrene standards)
[c] Estimated based on the intensities of proton signals in each ^1H n.m.r. without consideration of Me_2Si units or polymer ends
[d] A certain number of Si–H and Si–Cl groups were present in the polymers

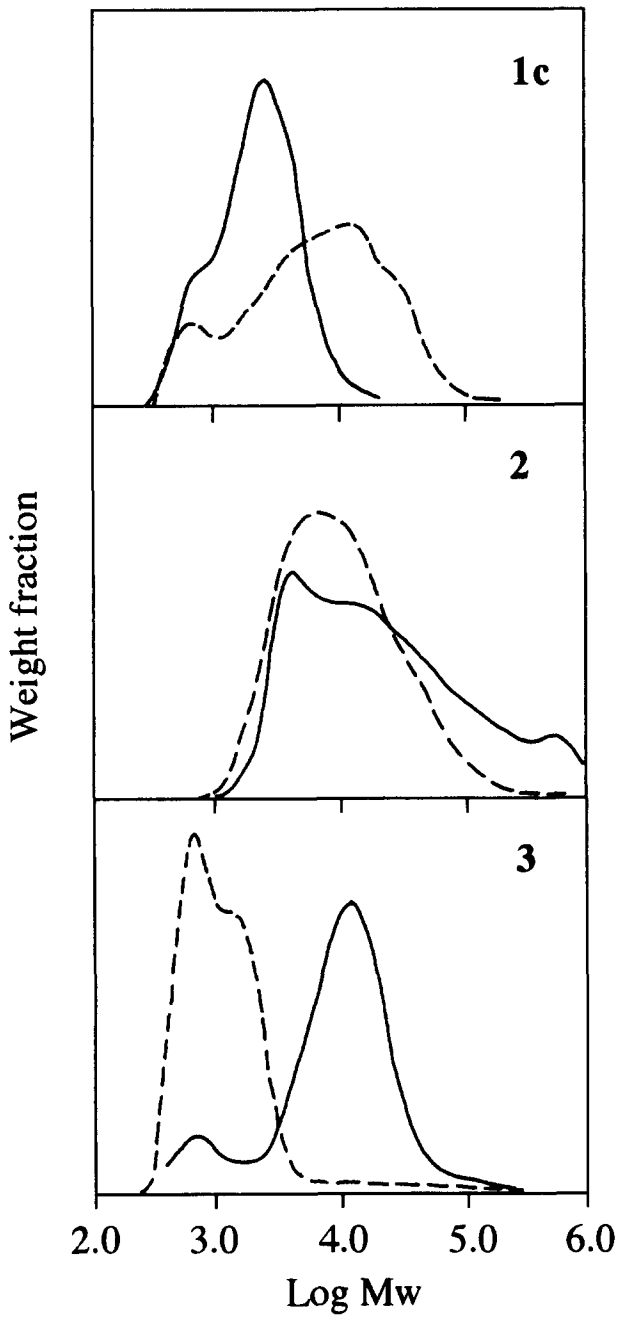

Figure 5 S.e.c. chromatograms of **1c** (top), **2** (middle) and **3** (bottom) using a refractive index detector before (solid line) and after irradiation (broken line) for 20 min under an inert atmosphere

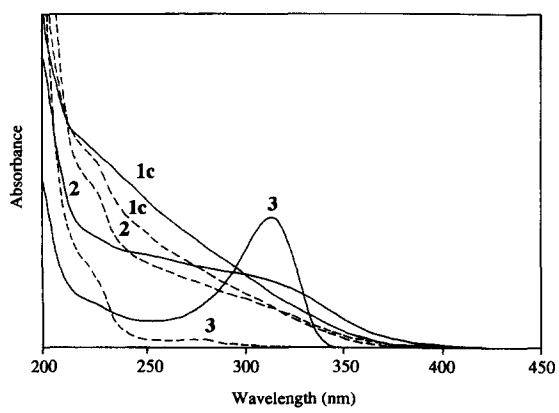

Figure 6 U.v. absorption spectra of **1c**, **2** and **3** before (solid line) and after irradiation (broken line) for 20 min under an inert atmosphere (9.4 mg l^{-1} in hexane)

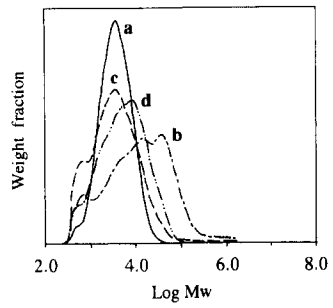

Figure 7 S.e.c. chromatograms using a refractive index detector for the photoreaction of **1e** in the presence or in the absence of silylene trappers: (a) before irradiation; (b) irradiation for 20 min in the absence of a silylene trapper; (c) irradiation for 20 min in the presence of trimethylethoxysilane; (d) irradiation for 20 min in the presence of triethylsilane

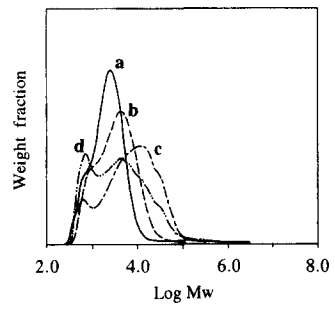

Figure 8 S.e.c. chromatograms using a refractive index detector for the photoreaction of **1c** with different irradiation time: (a) before irradiation; (b) irradiation for 5 min; (c) irradiation for 20 min; (d) irradiation for 60 min

wider. However, the photoreaction shifted that of **2** and **3** to the lower molecular weight side. The ^{1}H n.m.r. spectrum of the product obtained after removal of the volatile materials from the photoreaction mixture of **1c** was almost identical with that of the starting polymer, and even the integral ascribed to the ethoxy signals. The i.r. spectrum after the photoreaction was also identical with that of **1c**, except for the appearance of a peak at 2090 cm^{-1}, which is ascribed to the Si–H bond. Silanols could not be formed during the reaction in the absence of oxygen; therefore, the reaction of the silanols with alkoxysilyl groups could not occur, and ethanol would not be released from the polysilane polymer. From these observations, a kind of redistribution reaction of the polysilane polymer involving the formation of silylsilylenes[11] containing Si–Si chains and the insertion of the silylenes into the alkoxy–silicon bonds was considered to be the main reason for the increase in molecular weight and expansion of the distribution. The formation of silyl radicals was suggested by the generation of the Si–H bonds, and this is known to give rise to the decomposition of the polymer. But the extent of the degradation in **1c** arising from the silyl radical formation seemed to be small, because the molecular weight of **1c** did not reduce in practice. The silyl radicals generated from the photolysis of the network polysilanes such as **1c** and **2** would tend to recombine again rather than separate each other.

In order to confirm the reaction of silylenes with ethoxysilyl groups, quenching experiments were carried out. A hexane solution of **1e** was irradiated for 20 min in the presence of an excess amount of trimethylethoxysilane, which was reported as a silylene trapper[25]. The

peak of molecular weight distribution of the product was almost the same value, although the distribution became wider, as shown in *Figure 7*. This result indicated that the silylenes are trapped by trimethylethoxysilane, and the increase in molecular weight was suppressed. Then, **1e** was irradiated in the presence of an excess amount of triethylsilane, which is also known as a silylene trapper[22]. In this case the molecular weight of the products slightly increased after the reaction. The i.r. analysis of the resulting polymer exhibited the Si–H absorption band at 2090 cm^{-1}, which intensity was apparently greater than that of the product obtained from the photoreaction in the absence of triethylsilane. On the other hand, no Si–H compound was detected except for triethylsilane in g.c.–i.r.–m.s. analysis of volatile compounds in the reaction mixture. Consequently, the increase in molecular weight of the network ethoxypolysilanes was considered to be mainly ascribable to the reaction of silylenes with ethoxysilyl groups.

Molecular weight distributions of **1c** with different irradiation times are illustrated in *Figure 8*. After an irradiation of 5 min, the molecular weight slightly increased and the polydispersity became greater. These changes were expanded by the irradiation for 20 min. After a 60 min-irradiation, on the contrary, the molecular weight decreased compared with that of the product obtained after a 20 min-irradiation. Some part of the product after a 60 min-irradiation still had a greater molecular weight than the initial polymer. Therefore, the increase in molecular weight of the network ethoxypolysilane did not proceed infinitely.

CONCLUSIONS

Photoreaction of ethoxypolysilanes was investigated in the presence and in the absence of oxygen, and was compared with that of the alkylpolysilanes. The photoreaction of network ethoxypolysilanes in the presence of oxygen led to their photooxidation, and resulted in a decrease in molecular weight and a disappearance of the u.v. absorption. The decrease in the molecular weight of network ethoxypolysilanes was slower than the alkylpolysilanes, though the disappearance of the u.v. absorption around 315 nm of the ethoxypolysilanes was faster than that of polysilyne, and slower than that of polysilylene. The reason for this phenomenon could be explained by the reaction of the ethoxysilyl groups with silanols produced via silylenes and silyl radicals. On the other hand, the irradiation of ethoxypolysilanes at 254 nm in the absence of oxygen caused an increase in molecular weight. These results could also be explained by the influence of the alkoxysilyl group in the polysilane. The silylene formed by photolysis was inserted into the Si–OR bond, and this would retain the decomposition of the polymer chains.

Consequently, network methylethoxypolysilanes prepared by the disproportionation reaction of methylethoxydisilanes, which have the network degree between the polysilyne and polysilylene, would be a better candidate for photolithographic application for making electrical conducting patterns than polysilynes and polysilylenes.

ACKNOWLEDGEMENTS

This work was performed by Toshiba Silicone Co., Ltd. under the management of the Japan High Polymer Center as a part of the Industrial Science and Technology Frontier Program supported by the New Energy and Industrial Technology Development Organization.

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