

# Effect of backbone structures of polysilanes on the photooxidation reaction

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Photooxidation reactions of linear polysilanes [poly(cyclohexylmethylsilylene) and poly(methylphenylsilylene)], a network polysilane [poly(hexylsilylene)] and branched polysilanes [poly(cyclohexylmethylsilylene-*co*-phenylsilylene) and poly(cyclohexylmethylsilylene-*co*-hexylsilylene)] were investigated both in solution and in the solid state in the presence of oxygen. The reactions were monitored by u.v. and i.r. spectroscopies and size exclusion chromatography. Polysilanes containing a greater number of silylene units, i.e. highly branched polysilanes, required a greater dose of u.v. exposure for the completion of the photooxidation, which was determined by a decrease in the intensity of the polysilane's characteristic u.v. absorption and an increase in the intensity of the siloxane's i.r. absorption. The molecular weight change of the polymers also depended on the backbone structure. The degradation of the network and branched polysilanes was slower and smaller than that of linear polymers during the reactions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polysilane; photooxidation; structure)

## INTRODUCTION

Polysilanes have attracted considerable attention due to their unusual electronic and photophysical properties<sup>1,2</sup>, as well as their potential applications as photoresists<sup>3</sup>, photoconductors<sup>4</sup> waveguides<sup>5</sup> and non-linear optical materials<sup>6</sup>. For some of these applications, the photochemical stability of the materials was considered to be one of the most important requirements because polysilanes are known to be photo-reactive. There are some reports about the influence of backbone structures on the photochemical behaviour under an inert atmosphere<sup>7,8</sup>, and a network polysilylene was reported to be more photo-stable than a linear polysilylene<sup>9</sup>. For the photooxidation reaction, the network polysilylene was found to be difficult to degrade, whereas the linear polysilylene was degraded easily and generated smaller cyclic oligomers<sup>9</sup>.

We made a series of polysilanes that have different backbone structures such as linear, network and branched. These polysilanes were irradiated in solution and in the solid state using mercury arc lamps in the presence of oxygen, the conditions which are considered to be close to practical use. The reaction in solution was monitored by a change in the polysilane's characteristic u.v. absorption and molecular weight distribution. The reactions in the solid state were monitored by u.v. and i.r. absorption spectroscopies. From these analyses, we determined the correlation of the backbone structure of the polysilanes with photo-stability. In this paper, we report a significant effect of the backbone structures of the polysilanes on an amount of exposure dose for the

completion of the photooxidation and on the molecular weight change.

## EXPERIMENTAL

### Materials

Poly(cyclohexylmethylsilylene) and poly(methylphenylsilylene) were prepared by the Wurtz-type coupling reaction of the corresponding diorganodichlorosilanes with highly dispersed molten sodium metal in dry toluene at 110°C. A series of poly(cyclohexylmethylsilylene-*co*-phenylsilylene)s and poly(cyclohexylmethylsilylene-*co*-hexylsilylene) were prepared by similar procedures, using mixtures of cyclohexylmethyldichlorosilane and phenyltrichlorosilane or hexyltrichlorosilane, respectively. Poly(phenylsilylene) and poly(hexylsilylene) were prepared by almost the same procedures except for the addition of a small amount of 18-crown-6 ether using phenyl- or hexyl-trichlorosilane<sup>10</sup>. Polysilanes were purified by reprecipitation using methanol-toluene mixed solvents and then the molecular weight distributions of the polymers were determined by size exclusion chromatography (s.e.c.), based on monodispersed polystyrene standards. The characterization and ratios of the units were determined by <sup>1</sup>H and <sup>29</sup>Si n.m.r. spectroscopy. Hexane, which was dehydrated by sodium, was used as a solvent for the photooxidation reactions. Oxygen gas (purity: over 99.95%) was dehydrated by passage through a calcium chloride drying tube just before introduction to the reaction mixture.

### Measurements

The photooxidation of polysilanes in hexane solution (0.50 g l<sup>-1</sup>) were carried out using a low pressure

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mercury-arc lamp (32 W, Riko-Kagaku Sangyo Co. Ltd) with a stream of dry oxygen gas ( $1.7 \text{ ml s}^{-1}$ ). Polysilane films ( $\approx 0.70 \mu\text{m}$  thickness) were prepared on quartz plates for u.v. measurements and on KBr plates for i.r. measurements using 5–15 wt% toluene solutions by the spin-coating technique. The photooxidation of the polysilane films were performed using a high pressure mercury-arc lamp (80 W) in air. The integral exposure of u.v. light was measured using ORC UV-M30 instruments with a UV-35 sensor. The progress of the photooxidation reactions were monitored by u.v.-vis. absorption spectroscopy (Hitachi U-3500 spectrometer) and s.e.c. with a Jasco 870 u.v. detector at 254 nm and a Jasco 830 refractive index (RI) detector, and the data were based on monodispersed polystyrene standards with chloroform as the eluent. The  $^1\text{H}$  and  $^{29}\text{Si}$  n.m.r. spectra were measured using a Bruker ARX400 spectrometer with tetramethylsilane as external standard. The i.r. spectra were measured on a Shimadzu IR-47 infrared spectrometer. All experiments were carried out at room temperature.

## RESULTS AND DISCUSSION

All polymers were prepared by the Wurz-type coupling reaction of the corresponding diorganodichlorosilanes and organotrichlorosilanes. Newly developed procedures were less satisfactory for obtaining polysilanes with various backbone structures<sup>1</sup>. Of the various polysilanes, homo- (**1** and **5**) and copolymers (**2–4**), consisting of a cyclohexylmethylsilylene unit and phenylsilylene unit, were chosen for this work due to their relative ease of determination of the polymer composition ratio by  $^1\text{H}$  n.m.r. on the basis of the methyl proton and phenyl proton signals. In order to evaluate the influence of the phenyl group, poly(cyclohexylmethylsilylene-*co*-hexylsilylene) (**6**), poly(hexylsilylene) (**7**) and poly(methylphenylsilylene) (**8**) were also prepared. The characterization of the polysilanes is summarized in Table 1. The ratios of the silylene unit and silyne unit corresponded well to those of the monomer feeding ratios. The molecular weight of the copolymers was somehow relatively small<sup>8</sup>. The u.v. absorption spectra of the polysilanes are shown in Figure 1. The u.v. spectrum of **5** was measured in toluene because of its low solubility in hexane. The linear polysilanes **1** and **8** showed a sharp  $\sigma\text{--}\sigma^*$  absorption band. The branched or

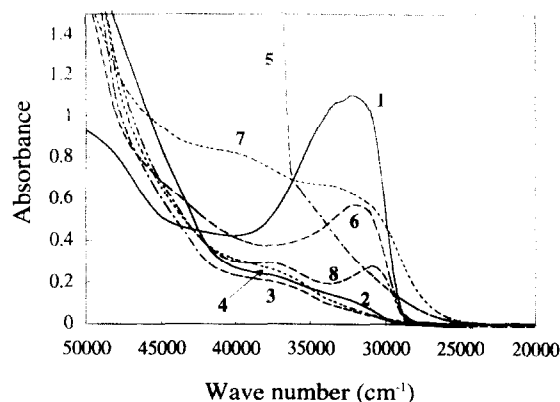


Figure 1 U.v.-vis. absorption spectra of **1**, **4** and **6–8** in hexane ( $1.0 \times 10^{-4} \text{ g l}^{-1}$ ) and **5** in benzene ( $1.0 \times 10^{-4} \text{ g l}^{-1}$ )

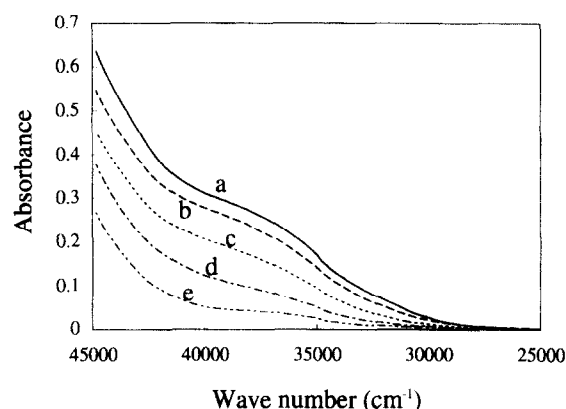


Figure 2 U.v. absorption spectra of **4** in hexane before and after irradiation (reaction mixtures were diluted 40 times with hexane): (a) before irradiation; (b) irradiation for 120 s; (c) 300 s; (d) 600 s; (e) 1200 s

network polymers (**2–7**) showed a broad u.v. absorption band without an obvious absorption maximum, and the absorption edge generally reached  $25\,000 \text{ cm}^{-1}$  ( $400 \text{ nm}$ )<sup>9</sup>.

The irradiation of each polysilane solution using a low pressure mercury-arc lamp in the presence of oxygen led to a gradual decrease in the intensity of the absorption bands in the u.v. region, indicating that cleavage of the Si–Si bonds occurred during irradiation. An example of the u.v. spectral change for the photooxidation of copolymer **4** is shown in Figure 2. After 1200 s

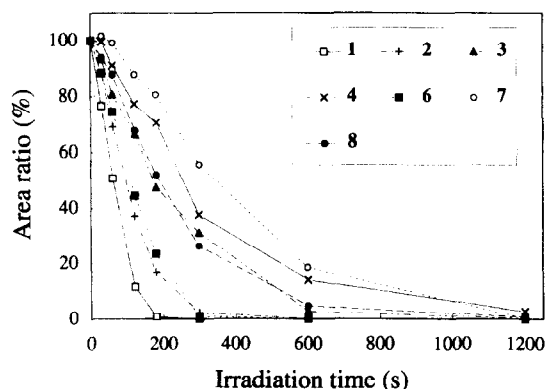
Table 1 Characterization of polysilanes

Polymer no.	Monomers and feeding ratio (mole fraction)	$M_w$ ( $M_w/M_n$ )	Polymer unit ratio (mole fraction)	Appearance
	CyclohexylMeSiCl <sub>2</sub> /PhSiCl <sub>3</sub>		CyclohexylMeSi/PhSi	
<b>1</b>	(1.0)/(0.0)	23000 (2.2)	1.0/0.0	White solid
<b>2</b>	(0.90)/(0.10)	1200 (1.7)	0.89/0.11	Brown sticky solid
<b>3</b>	(0.75)/(0.25)	1200 (1.7)	0.77/0.23	Brown sticky solid
<b>4</b>	(0.50)/(0.50)	1900 (2.2)	0.48/0.52	Yellow solid
<b>5</b>	(0.0)/(1.0)	2500 (1.3)	0.0/1.0	Yellow solid
	CyclohexylMeSiCl <sub>2</sub> /HexSiCl <sub>3</sub>		CyclohexylMeSi/HexSi	
<b>6</b>	(0.50)/(0.50)	4500 (1.6)	0.59/0.41	Yellow solid
<b>7</b>	(0./0)/(1.0)	25800 (4.2)	0.0/1.0	Yellow solid
<b>8</b>	PhMeSiCl <sub>2</sub> only		PhMeSi only	
	(1.0)	7900 (2.9)	1.0	White solid

irradiation, the i.r. spectrum of the reaction mixture showed two new absorption bands around 3300 and 1100  $\text{cm}^{-1}$  which were ascribed to the Si-OH and Si-O-Si bonds, respectively.

The u.v. absorption of the branched or network polysilanes have no apparent absorption maxima as shown in *Figure 1*; therefore, we calculated each integrated u.v. absorbance between 33 000 and 25 000  $\text{cm}^{-1}$  including the linear polysilanes and plotted the ratios based on the absorptions before irradiation as a function of irradiation time in *Figure 3*. The absorptions of the region were considered to be mainly contributed by the  $\sigma-\sigma^*$  transition of Si-Si bonds. The contribution of  $\pi-\pi^*$  transition of phenyl groups would be mostly excluded. When comparing these curves in order to determine their photo-stability, there were some problems. First, the absorption coefficient of each polymer was different based on substituents<sup>1,11</sup> and chain lengths<sup>1,12</sup>. Second, the coefficient would change as the photooxidation reaction proceeded because the contiguous Si-Si bonds length was shortened by the insertion of an oxygen into the Si-Si bonds. Nevertheless, we concluded that we could compare the photochemical behaviour of these similar polymers for obtained relative properties as materials, because the differences in the coefficients were not large and in the range 3000–10 000 for typical linear polysilanes<sup>1,11</sup>, and changes of each coefficient and  $\lambda_{\text{max}}$  during the photooxidation were gradual<sup>1,2</sup>. The u.v. spectral changes of poly(cyclohexylmethylsilylene) and poly(cyclohexylmethylsilylene-co-methylphenylsilylene) were reported to be almost identical<sup>12</sup>.

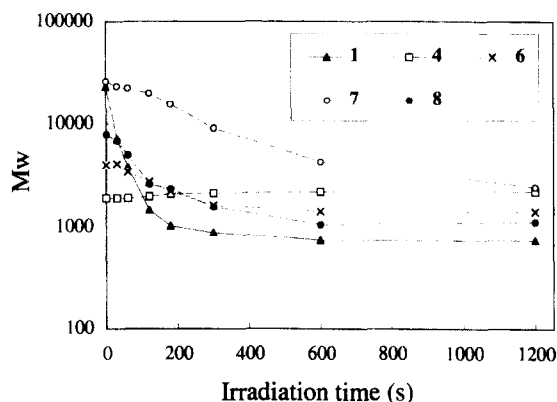
Comparing polysilanes 1–4, which consisted of a cyclohexylmethylsilylene unit and a phenylsilylene unit, the bleaching rate of u.v. absorption for polysilanes decreased as the ratio of the phenylsilylene units increased, i.e. branched polysilanes required a greater dose of u.v. exposure for the completion of the photooxidation. The order of the photo-bleaching rate was the same in the case of all alkylpolysilanes 1, 6 and 7, suggesting the nature of the backbone structure would be the main factor influencing the bleaching rate. The silyl radicals and silylenes formed by a photo-scission of the network and branched polymers would have a tendency to recombine again before the reaction with oxygen because of the so-called cage effect.



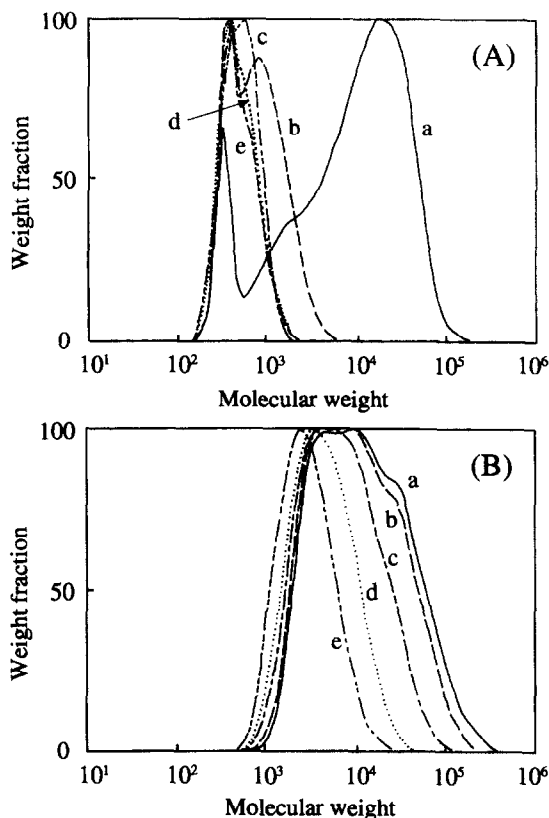
**Figure 3** Variation in u.v. absorption area of 1–4 and 6–8 for the photooxidation reaction in solution. The ratios were calculated by the area between 33 000 and 25 000  $\text{cm}^{-1}$  of each absorption and based on each absorption before irradiation

Phenyl groups in the polysilanes also affected the amount of u.v. exposure dose. Bleaching rates of u.v. absorption for 8 and 4, both polysilanes having phenyl groups, were slower than that of alkyl substituted polysilanes 1 and 6, respectively. This is probably because the phenyl groups absorbed u.v. light around 254 nm. Another reason would be that the u.v. absorption of the polymer containing the Si-C<sub>6</sub>H<sub>4</sub>-Si moiety, formed by a photo-induced rearrangement<sup>13,14</sup> or the reaction of silyl radicals with phenyl groups<sup>15</sup>, was observed in almost the same u.v. region of the original polysilanes<sup>16–18</sup>. The rate of bleaching for the linear polymer 8 was close to that for the copolymer 3, which had 23% of phenylsilylene units, faster than that for copolymer 6 and slower than that for the network polymer 7. These results indicated that both the branching of the polymer backbone and increasing the number of phenyl groups in the polymers could influence the rate of photooxidation strongly.

A comparison of molecular weight changes was analysed by s.e.c. using a u.v. detector. The RI detector was also used for alkylpolysilanes because polysilanes were converted into polysiloxane, which does not have an absorption in the u.v. region. The weight-average molecular weight (vs. polystyrene standards) of some polymers were plotted as a function of irradiation time in *Figure 4*. Comparing alkylpolysilanes 1 and 7, the polymer degradation of 7 was much slower than that of 1. The molecular weight of 1 was below 1000 after irradiation for 180 s whereas that of 7 was over 15 000 although these two polymers had almost the same initial molecular weight. The molecular weight distributions of 1 and 7 are shown in *Figures 5A and B*. The polydispersities of the two polymers became smaller along with the progress of the photooxidation. After a 20 min photooxidation reaction, the network polysilane 7 eventually degraded to smaller molecules. The polymer degradation of linear polysilane 8 proceeded with a short irradiation time, but the final molecular weight was higher than that of 1. This result indicated that the branching of the polymer backbone involving the phenyl groups might occur to some extent; however, the influence of the phenyl group was small on preventing its degradation. The changes of the molecular weight and polydispersity of branched polysilanes 2–4 were not observed significantly during the photooxidation. The



**Figure 4** Variation in the weight-average molecular weights (vs. polystyrene standards) of 1, 4 and 6–8 for the photooxidation reactions in solution

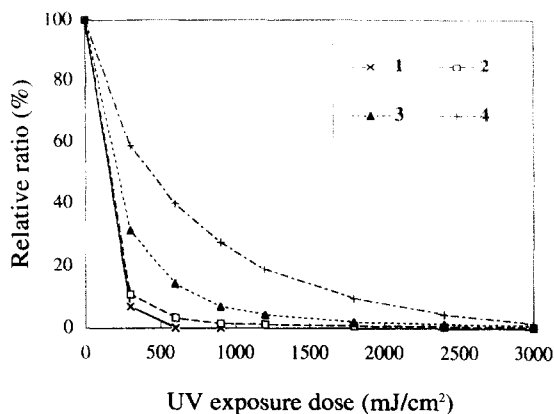


**Figure 5** Weight-average molecular weight distribution (vs. polystyrene standards) of **1** shown in (A) and **7** shown in (B) for the photooxidation reactions in solution: (a) before irradiation; (b) irradiation for 120 s; (c) 300 s; (d) 600 s; (e) 1200 s

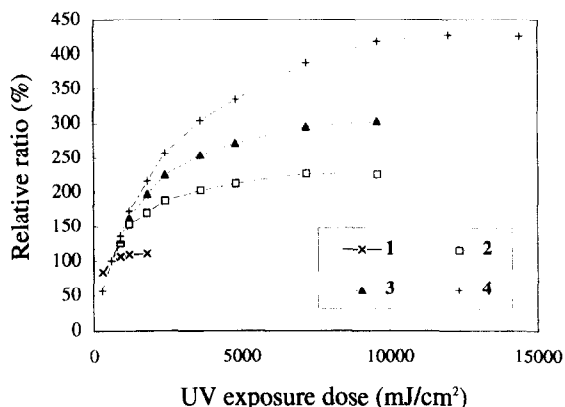
changes in molecular weight of **4** are illustrated in *Figure 4*. These results may be caused by the low initial molecular weight of the branched polysilanes. The resistance of the network polysilane **7** and the branched polysilane **6** to the degradation could be explained by the network or branched structure of the polymer backbone. That is, even if one Si-Si bond in **7** could be cleaved by the photo-reaction, the molecular weight of the polymer would not change because the polymer chain was crosslinked. In this respect, the branched or network polymer is more stable as a material than the linear polysilanes.

We investigated the photo-stability of the polysilanes in the solid state. Polysilane films of **1-4**, which were prepared on quartz plates for u.v. measurement and on KBr plates for i.r. measurement, were photolysed in air using a high-pressure mercury-arc lamp. The u.v. spectral changes were plotted in the same manner as the photooxidation shown in solution in *Figure 6*. Again, the photo-bleaching rates were dependent on the branching degree, and the order was the same as the solution experiments.

The progress in the photooxidation reaction of the polysilane films were determined by increments of the absorption band around  $1050\text{ cm}^{-1}$ , which was ascribed to the Si-O bond. We made the assumption that the extinction coefficient of the siloxane absorption band is independent of the degree of the photooxidation and the substituents. The siloxane absorption intensity was evaluated in terms of area obtained by subtracting the original spectrum from the photo-irradiated one. The



**Figure 6** Variation in u.v. absorption area of **1-4** for the photooxidation reaction in the films. The ratios were calculated by the area between  $33\,000$  and  $25\,000\text{ cm}^{-1}$  of each absorption and based on each absorption before irradiation



**Figure 7** Variation in increments of siloxane's absorption band between  $\approx 950$  and  $1150\text{ cm}^{-1}$  of **1-4** for the photooxidation reaction in the films. The ratios were based on the increments of the siloxane's absorption at  $600\text{ mJ cm}^{-2}$  irradiation

siloxane content, which increased with increasing irradiation time, was obtained by normalizing the area with the increment of the absorption band of each polysilane with irradiation of  $600\text{ mJ cm}^{-2}$  taken as a 100% criterion. The results are summarized in *Figure 7*. The increment of the siloxane's absorption of **1** was almost saturated by the  $600\text{ mJ cm}^{-2}$  exposure dose, but that of **4** required  $10\text{ J cm}^{-2}$ . The order of increments of saturation was consistent with the degree of branching of the polymers. These data suggested that branched polysilanes were more photo-stable than the linear polymers.

### CONCLUSIONS

Photooxidation reactions of polysilanes with different backbone structures were investigated both in solution and in the solid state in the presence of oxygen. We found that the backbone structure of the polysilanes significantly affected the rate of photooxidation and that the polysilanes containing a greater number of silyne units required greater doses of u.v. exposure for the completion of the photooxidation. The degradation of network and branched polysilanes was slower and smaller than that of linear polymers during the reactions. These data suggest that the network and branched polysilanes were

more photo-stable as a material than the linear polymers.

#### ACKNOWLEDGEMENTS

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