Studies on the Laser Degradation of the CHCl₃ Solution of Polysilane

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ABSTRACT: In this paper, the XeCl excimer laser was used to irradiate the CHCl₃ solution of polymethylphenethylsilane (PMPES) and that of poly(dimethylsilane-*co*-methylphenethylsilane) (PDM-MPES). The laser energy absorbed by the polysilane macromolecules was measured, the gel permeation chromatography molecular weights of the polysilane macromolecules both before and after irradiation were determined, and their corresponding apparent quantum yields under the irradiation were calculated. The apparent quantum yield of laser degradation of the CHCl₃ solution of PMPES is two orders of magnitude larger than that of the CHCl₃ solution of PDM-MPES, indicating that the spatial obstruction of the substituents attached to the polysilane chains has great effect on its apparent quantum yield of laser degradation. For the polysilane photodegradation under a rather low laser energy, with the increase of the laser energy absorbed by the polysilane macromolecules, the average molecular weight after irradiation decreases gradually while the average scissions per macromolecule and the apparent quantum yield increase. The concentration of the CHCl₃ solution of polysilane has only small effect on its apparent quantum yield of laser degradation. According to the X-ray photoelectron spectroscopy analysis, the CHCl₃ solvent is involved in the photoreaction and combined into the dissociated product. In light of the references, it is preliminarily proposed that the laser degradation of the CHCl₃ solution of polysilane may result from the comprehensive action of such factors as homolytic cleavage, silylene extrusion, chain cleavage by reductive elimination, the radical chain transfer process, the fluorescence quenching of polysilane by CHCl₃, etc. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1515–1519, 1997

Key words: polysilane; excimer laser; photodegradation; apparent quantum yields

INTRODUCTION

In the early 1980s, the synthesis of soluble high-molecular-weight polysilanes resulted in studies on their high performances.[1,2] Polysilane, because of its Si—Si σ conjugation in the main chain, has many unique optical and electrical properties and, in the past 15 years, has undergone rather deep investigation in many aspects such as high resolution microlithography,[3] nonlinear optics,[4] photoconductivity,[5] optical waveguide,[6] etc.

For all soluble high-molecular-weight polysilanes, there exists strong and wide ultraviolet (UV) absorption. After the UV absorption, a so-

called "photobleaching" occurs and the polysilane Si—Si main chains are broken into fragments.[7] The photobleaching of polysilanes is the most important theoretical foundation for their high resolution microlithography,[3] etc.

R. D. Miller and colleagues have succeeded in greatly improving the photodegradation rate of the polymethylphenylsilane (PMPES) film by adding aromatic sensitizers with —CCl_3,[8] which is of theoretical and practical importance in the study of polysilane microlithography. In this paper, the authors have studied the laser degradation of the $CHCl_3$ solution of polysilane, and in combination with the UV, gel permeation chromatography (GPC), X-ray photoelectron spectroscopy (XPS), and other analyses, obtained some very interesting results.

EXPERIMENTAL

Materials

PMPES and poly(dimethylsilane-*co*-methylphenethylsilane) (PDM-MPES) were synthesized by Wurtz-type reductive condensation of the corresponding disubstituent dichlorosilane monomers[9,10] and purified according to the literature procedures. The copolymerization ratio (m/n) for PDM-MPES was 1.25. The $CHCl_3$ solvent was analytically pure and further purified before use according to the reported methods.[11]

Instrumentation

The laser source was supported by a XeCl 400XR Excimer Laser System. An LPE-1A Laser Power/Energy Meter was used to determine the pulsed laser energy values. The UV absorption spectra were recorded by a PE Lambda 4B UV/Vis Spectrophotometer. The GPC molecular weights were measured by a Waters 486 (tunable absorbance detector at 254 nm) and the XPS analysis by an XSAM 800 Electron Spectrometer for Chemical Application.

The calculation of the concentrations of polysilane solutions was based upon the number of Si atoms.

The polysilane solutions were put in a quartz trough with windows and irradiated by the XeCl excimer laser (λ = 308 nm). The pulsed laser energy values were determined. The UV, XPS, and GPC experiments were all conducted both before and after irradiation.
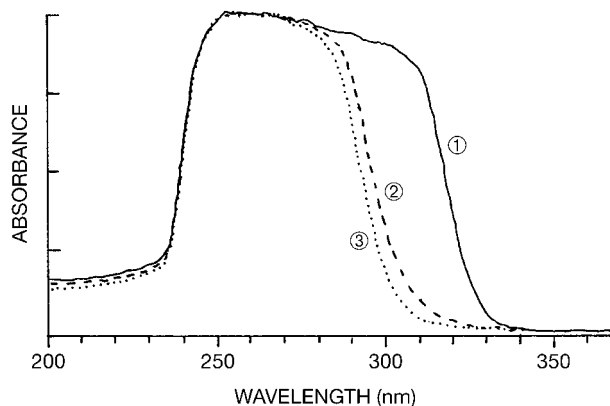
Figure 1 The UV absorption spectra of the $CHCl_3$ solution of PDM-MPES under different doses of the XeCl excimer laser irradiation. Laser energy absorbed by 1 mL $3.30 \times 10^{-3}M$ $CHCl_3$ solution of PDM-MPES: (1) 0.000 J, (2) 1.110 J, and (3) 1.645 J.

RESULTS AND DISCUSSION

Under the XeCl excimer laser irradiation, with the increase of the incident energy, the absorption band near 300 nm for the Si—Si segments in the $CHCl_3$ solution of PDM-MPES weakened step by step and the maximum absorption wavelength shifted to the blue range, i.e., the "photo-bleaching" phenomenon appeared, as shown in Figure 1. From Figure 1, it can be seen that photodegradation has indeed occurred for the polysilane macromolecules. This is also demonstrated by the GPC molecular weight analysis listed in Table I.

By measuring the incident energy and the transmittent energy of the trough with the $CHCl_3$ solutions of polysilanes and that with only the $CHCl_3$ solvent, the actual laser energy absorbed by the polysilane macromolecules was obtained. The molecular weights both before and after irradiation were determined, from which the average scissions of the polysilane macromolecules under the irradiation were calculated.

Since the energy per mole of photons at 308 nm is 388 kJ mol^{-1}, far greater than that per mole of Si—Si bonds (197 kJ mol^{-1}), theoretically, we think, one photon at 308 nm is enough to cut off one Si—Si bond. Furthermore, according to the reactional threshold experiment, laser irradiation with an incident energy density of 178 mJ cm^{-2} can obviously bleach the characteristic absorption band of PMPES after passing through a 20-layer attenuator (transmissivity per layer: 0.5823) and an incident quartz window (transmissivity: 0.851). The reactional threshold should be

Table I   Apparent Quantum Yields of Laser Degradation of the CHCl₃ Solutions of PMPES and PDM-MPES

Solutions	1[a]	2[b]	3[b]	4[b]	5[c]
$\overline{MW}_0$	8,995	6,799	6,799	6,799	6,799
$\overline{MW}$	1,013	3,001	2,340	1,455	2,460
Average number of photons absorbed by every macromolecule	1.37	111	147	196	62.7
Average scissions per macromolecule	7.88	1.27	1.91	3.67	1.76
Apparent quantum yield (%)	575	1.14	1.30	1.87	2.81

1, CHCl₃ solution of PMPES; 2–5, CHCl₃ solutions of PDM-MPES.
[a] $2.43 \times 10^{-3}M$.
[b] $3.30 \times 10^{-3}M$.
[c] $3.30 \times 10^{-2}M$.

$$178 \times 0.5823^{20} \times 0.851 = 3.0 \times 10^{-3} \text{ mJ cm}^{-2}$$

Such a small threshold also indicates that the Si—Si scission process is probably a mono-photon one.

The apparent quantum yield is defined as the average scissions per macromolecule divided by the average number of photons absorbed by every macromolecule. Obviously, the definition of the apparent quantum yield lies mainly in the result of the laser degradation. The apparent quantum yields for solutions 1–5 are listed in Table I.

According to Table I, comparing solution 1 with the other solutions, it is obvious that the apparent quantum yield of laser degradation of the CHCl₃ solution of PDM-MPES is two orders of magnitude smaller than that of the CHCl₃ solution of PMPES, which is probably due to the difference in spatial obstruction between the substituents attached to the PDM-MPES chains and those to the PMPES chains. Through calculation, the ratio of the number of methyls attached to the PMPES chains to that of phenethyls to the PMPES chains is 1.00, while the ratio of the number of methyls attached to the PDM-MPES chains to that of phenethyls to the PDM-MPES chains is 3.50; that is, the spatial obstruction of the substituents attached to the PDM-MPES chains is much smaller than that of the substituents to the PMPES chains. Under such circumstances, the silyls produced by the PDM-MPES chain scission are possibly much easier to recombine than those produced by the PMPES chain scission, leading to the great difference between the apparent quantum yield of laser degradation of the CHCl₃ solution of PDM-MPES and that of the CHCl₃ solution of PMPES.

In Table I, from solution 2 to solution 4, we can see that for the same polysilane solution, for polysilane photodegradation under a rather low laser energy, with the increase of the laser energy absorbed by the polysilane macromolecules, the average molecular weight after irradiation decreased gradually while the average scissions per macromolecule and the apparent quantum yield increased. The increase of the apparent quantum yield may be related to the conformation of the polysilane segments in the random coils of the polysilane macromolecules. Possibly, the polysilane photodegradation under a rather low laser energy liberates some twists and kinks in the polysilane chains between which polysilane chains exist as planar zigzagged segments,[12,13] and turns part of them into new zigzagged segments or lengthens some already existent zigzagged segments. These new or lengthened zigzagged segments more easily absorb the UV light, degrade, and make the apparent quantum yield increase. Of course, obviously, further photodegradation will make the zigzagged segments shorter until they are unable to absorb the UV light and be degraded.

In Table I, comparing solutions 2, 3, and 4 with solution 5, we can also see that for the same polysilane copolymer PDM-MPES, the concentration of its CHCl₃ solution has only a small effect on its apparent quantum yield.

The results of the XPS analysis are shown in Table II. From Table II, we can see that the C/Si atomic number ratio after irradiation increases and the Cl element appears in the photoscissored product. Moreover, with the increase of the laser energy, both the C/Si atomic number ratio and

Table II Results of the XPS Analysis of PMPES and PDM-PMPES Before and After Irradiation

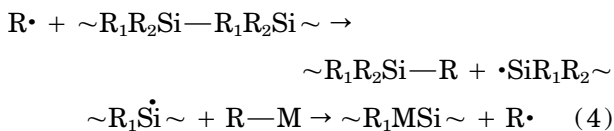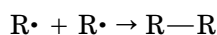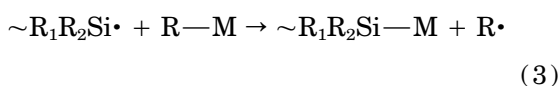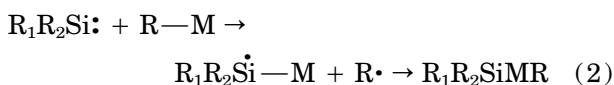| Solution	1[a]	2[b]	3[b]	4[b]
C/Si atomic number ratio before irradiation	8.90/1	2.95/1	2.95/1	2.95/1
C/Si atomic number ratio after irradiation	9.34/1	3.01/1	3.20/1	3.26/1
Cl/Si atomic number ratio after irradiation	0.104	0.00248	0.00546	0.0109

1, $CHCl_3$ solution of PMPES; 2–4, $CHCl_3$ solutions of PDM-MPES.

[a] $2.43 \times 10^{-3} M$.

[b] $3.30 \times 10^{-3} M$.

the Cl/Si atomic ratio in the product increase. All these indicate that under the laser irradiation, the $CHCl_3$ solvent is involved in the photoreaction and combined with the dissociated polysilane fragments.

Karatsu and associates have made systematic researches on the photodegradation mechanism of polysilane $[R_1R_2Si]_n$ in its cyclohexane solution and put forward three processes[14]: (1) silylene ($R_1R_2Si\colon$) extrusion; (2) homolytic cleavage into radicals ($\sim R_1R_2Si\cdot$); and (3) chain cleavage by reductive elimination into disylsilylenes ($\sim R_1Si\colon$) and polysilanes with shorter chains ($R_1R_2Si\sim$), in which the former change into silyldisilenes ($\sim SiR_1{=}SiR_1R_2$), which are combined with radicals ($\sim R_1R_2Si\cdot$) and form persistent radicals ($\sim S\overset{\bullet}{i}R_1 SiR_1R_2SiR_1R_2\sim$). So the reactions of polysilane ($\sim R_1R_2Si\sim$) under UV irradiation may produce three kinds of radicals and these radicals may react with the solvents ($R{-}M$), described as follows:

$$\sim R_1R_2Si{-}R_1R_2Si{-}R_1R_2Si\sim \rightarrow$$
$$R_1R_2Si\colon + \sim R_1R_2Si\cdot + \sim R_1\overset{\bullet}{S}i\sim \quad (1)$$

$$R_1R_2Si\colon + R{-}M \rightarrow$$
$$R_1R_2\overset{\bullet}{S}i{-}M + R\cdot \rightarrow R_1R_2SiMR \quad (2)$$

$$\sim R_1R_2Si\cdot + R{-}M \rightarrow \sim R_1R_2Si{-}M + R\cdot$$
$$(3)$$

$$R\cdot + R\cdot \rightarrow R{-}R$$

$$R\cdot + \sim R_1R_2Si{-}R_1R_2Si\sim \rightarrow$$
$$\sim R_1R_2Si{-}R + \cdot SiR_1R_2\sim$$

$$\sim R_1\overset{\bullet}{S}i\sim + R{-}M \rightarrow \sim R_1MSi\sim + R\cdot \quad (4)$$
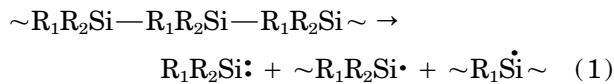
where M is perhaps $-H$ or $-Cl$. The actual process may be much more complicated.

The XPS analysis indicates that the $CHCl_3$ solvent not only participates in the reactions but also contributes rather largely. West has studied the photodegradation of some polysilanes and observed that the degradation process can be speeded by the addition of halogen compounds—transferring halogen to the silyl radicals and inhibiting recombination.[15] We tentatively propose that in the photodegradation of polysilane there may exist such a radical chain transfer process as described in reactions (2)–(4) above.

Li Gao-Quan and coworkers have studied the room-temperature cyclohexane solution fluorescence quenching of $1.0 \times 10^{-4} M$ PDM-MPES by $CHCl_3$ (excitation wavelength $\lambda_{ex} = 310$ nm) and observed that the fluorescence quenching intensity ratio F_0/F is about 3 when the concentration of $CHCl_3$ is at $5.00 M$.[16] The fluorescence quenching of polysilane by $CHCl_3$ results partially from the "outer heavy atom effect" of the halogen atoms. With the decrease of the population of the S_1 state of the polysilane segments, the population of the T_1 state increases,[17] which makes the $Si{-}Si$ bonds in the polysilane segments easier to scissor.[18] So the fluorescence quenching of polysilane by $CHCl_3$ may also be an important factor in the acceleration of polysilane photodegradation.

Overall, the laser degradation of polysilane in $CHCl_3$ may result from the comprehensive action of such factors as silylene extrusion, homolytic cleavage, chain cleavage by reductive elimination, the radical chain transfer process, the fluorescence quenching of polysilane by $CHCl_3$, etc. Of course, all these need further investigation. In any case, the studies on the apparent quantum yield of laser degradation of the polysilane solution are of guiding significance in the study of the high-resolution polysilane photoresists.

CONCLUSIONS

1. According to the UV spectra and GPC analysis of the $CHCl_3$ solution of polysilane both before and after the XeCl excimer la-

ser irradiation, the polysilane macromolecules have indeed been photodegraded.

2. From the calculation of the apparent quantum yield, the apparent quantum yield of laser degradation of the $CHCl_3$ solution of PDM-MPES is two orders of magnitude smaller than that of the $CHCl_3$ solution of PMPES, indicating that the spatial obstruction of the substituents attached to the polysilane chains has great effect on its apparent quantum yield of laser degradation. For the polysilane photodegradation under a rather low laser energy, with the increase of the laser energy absorbed by every macromolecule, the average molecular weight after irradiation decreases gradually while the average scissions per macromolecule and the apparent quantum yield increase. The concentration of the $CHCl_3$ solution of polysilane has only small effect on its apparent quantum yield.

3. The XPS analysis indicates that the $CHCl_3$ solvent participates in the photoreaction and is combined with the dissociated polysilane fragments.

4. The laser degradation of the $CHCl_3$ solution of polysilane may result from the comprehensive action of such factors as silylene extrusion, homolytic cleavage, chain cleavage by reductive elimination, the radical chain transfer process, the fluorescence quenching of polysilane by $CHCl_3$, etc.

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