Kinetic Analysis on Pyrolysis of Poly(methylphenylsilane)

Lujun Pan, Mei Zhang, and Yoshikazu Nakayama*

Department of Physics and Electronics, College of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

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Pyrolysis of poly(methylphenylsilane) in the states of powder, film, and photooxidized film has been studied by mass spectroscopy. The kinetic analysis of the evolution spectra of a unit of the polysilane CH_3−Si−C_6H_5 and one of substituents C_6H_5 gives the mechanism and activation energies of decomposition reactions. The thermal decomposition of poly(methylphenylsilane) is a type of depolymerization with random initiation. It is found that the activation energies of thermal decomposition have Gaussian distributions rather than keeping constant values. The activation energies of thermal decomposition in film are higher than that in powder because of its stronger interaction among the molecules. Due to the photodegradation and photoinduced oxidation of polysilane, photooxidized film has higher activation energies of decomposition and a broader distribution of activation energies than the unoxidized film.

Introduction

Polysilanes having linear Si−Si backbone are well-known as a new type of organopolymers which have wide applications such as thermal precursors to silicon carbide (SiC) and photoresists for microlithography.[1,2] The former began with Yajima and co-workers when they succeeded in converting poly(dimethylsilane) to SiC fiber with heat treatment in 1975.[3,4] Because of the photosensitivity and solubility, polysilanes have also been researched as a photoresist for microlithography.[1,2,5,6]

In these fields, high-temperature treatment and UV irradiation are very important processes. West reported that the UV irradiation of the related linear polydialkylsilanes in oxygen results in their rapid bleaching and photodegradation to low molecular weight siloxane fragments.[7] Watanabe and co-workers reported that heat treatment of poly(phenylsilyne) film under UV irradiation in air leads to its conversion to SiO_2.[8] Studies on the thermal decomposition of polysilanes are of extreme importance from a practical point of view. They not only explain the behavior of polysilanes under conditions of high temperatures, but also help in selecting the right kind of previously existing materials for specific uses where high temperatures are encountered, for example, the conversion to SiC. In the present research on pyrolysis of polysilanes, the results of thermogravimetric analysis (TGA) show that polysilanes are thermostable below 570 K, then have a drastic weight loss accompanying the chain scission and the evolution of volatile silicon compounds, and are stable once again after 770 K.[2,9] However, there are less reports concerned with the details of the evolved substances and the mechanism and the activation energies of thermal decomposition of polysilanes. In this paper, the pyrolysis of poly(methylphenylsilane) (PMPS) in the states of powder, film, and photoinduced oxidized film has been studied by mass spectroscopy. The kinetic analysis for the evolution of a unit of the polysilane CH_3−Si−C_6H_5 and one of substituents C_6H_5 was performed to determine the mechanism and the activation energies of thermal decomposition reactions. It is evidenced that the activation energies depend on the states of PMPS.

Experimental Section

Polysilane of PMPS was synthesized by condensation of methylphenyldichlorosilanes with sodium metal in reflux toluene at about 110 °C in the usual manner. The molecular weight, being 130 000, was determined by gel permeation chromatography using polystyrene for calibration. Polysilane films with a thickness about 0.2 μm were formed on quartz glass plates and crystalline silicon substrates by a spin-coating technique from a toluene solution.

The photoinduced oxidized film of PMPS was prepared by irradiation with high-pressure mercury lamp light (50 mW/cm^2) in air for 1000 s. The changes in ultraviolet (UV) and infrared (IR) absorption spectra of PMPS films by exposure to UV light are shown in Figure 1. Due to UV irradiation, absorption peaks relating to Si−Si main chains at 459 cm^{-1} in IR spectra and 336 nm in UV absorption spectra decreased, but the Si−O−Si bonds (around 1050 cm^{-1}) increased. Furthermore, absorption peaks[10] relating to methyl substituents at 697, 757, and 1247 cm^{-1} and phenyl substituents at 3068 and 1430 cm^{-1} in IR spectra, and the absorption peak at 278 nm relating to phenyl substituents in UV absorption spectra

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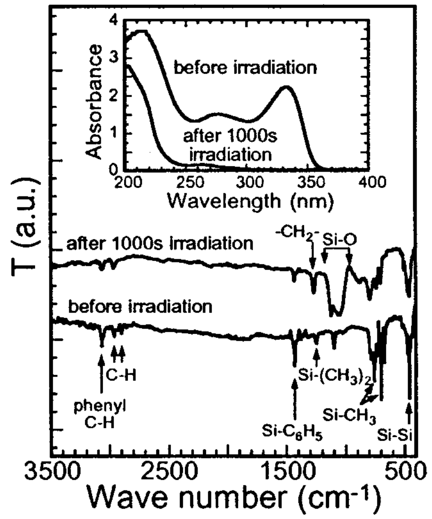

Figure 1. IR spectra of PMPS film before and after 1000-s irradiation by UV light in air. The inset shows the corresponding UV absorption spectra of PMPS film.

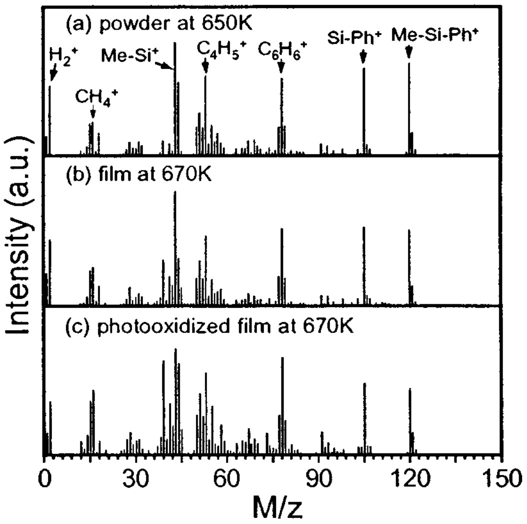

Figure 2. Mass spectra for PMPS in the states of (a) powder at 650 K, (b) film at 670 K, and (c) photooxidized film at 670 K.

decreased. After exposure to UV light, PMPS molecules were shortened and oxidized and part of them were converted to low weight siloxane fragments.[7]

Pyrolysis of PMPS in the states of powder, film, and photooxidized film was performed at the heating rate of 10 K/min, and the evolution of gases was measured by quadrupole mass spectrometer (QMS). The operating pressure of QMS was 1.2×10^{-6} Torr. To determine the mechanism of the thermal degradation, PMPS powder was also pyrolized at an isothermal condition of 563 K.

Results

Figure 2 shows the mass spectra of PMPS in the states of powder, film, and photooxidized film. The principal peaks observed are attributable to the following organosilicon ions: *M/z* 120, $(CH_3{-}Si{-}C_6H_5)^+$, arising from the fundamental unit of PMPS; *M/z* 105, $(Si{-}C_6H_5)^+$; *M/z* 43, CH_3Si^+; *M/z* 78, $C_6H_6^+$; and *M/z* 16, CH_4^+, associated with the cleavage of methyl and phenyl substituents. There is no signal between *M/z* 125 and 200, suggesting that the main product in pyrolysis of PMPS is monomer and the type of decomposition reaction is depolymerization. The detection of $C_6H_6^+$ and CH_4^+ indicates that the evolution of benzene and methane produced by the radical reactions of C_6H_5 and CH_3 with H_2 or H, respectively, on the sample surface rather than the decomposition of $CH_3{-}Si{-}C_6H_5$ followed by the radical reactions in the ionization chamber of QMS, because the second-order reactions are difficult to achieve in the high vacuum of 10^{-6} Torr. This is also noted by the result that the signal of $C_6H_6^+$ is not proportional to that of $(CH_3{-}Si{-}C_6H_5)^+$. Because the evolution of $CH_3{-}Si{-}C_6H_5$ and C_6H_6 directly reflect the respective cleavages of Si−Si main chains and phenyl substituents, the analysis of their evolution spectra gives us information on the decomposition process of PMPS.

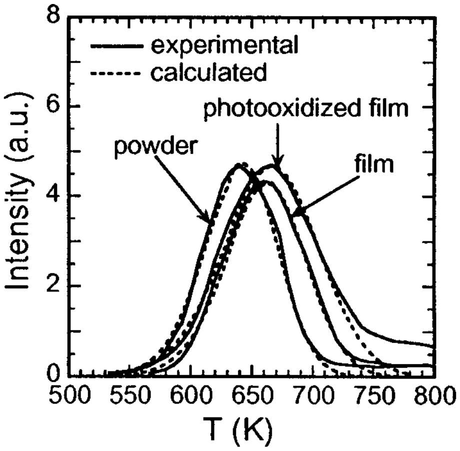

Figure 3. Evolution spectra of *M/z* 120, $CH_3{-}Si{-}C_6H_5$ from PMPS in the state of powder, film, and photooxidized film. The broken lines show the calculated curves.

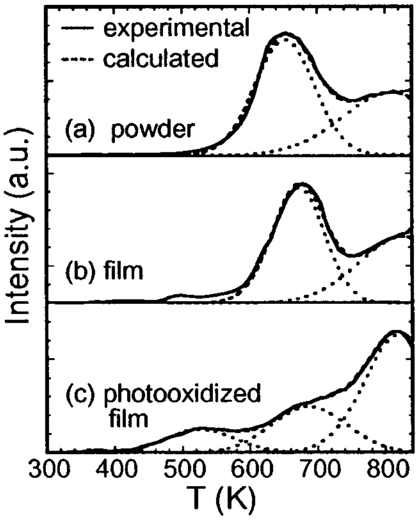

Figure 4. Evolution spectra of *M/z* 78, C_6H_6 for PMPS in the states of (a) powder, (b) film, and (c) photooxidized film. The broken lines show the calculated curves.

Figures 3 and 4 show the evolution spectra of *M/z* 120, $CH_3{-}Si{-}C_6H_5$ and *M/z* 78, C_6H_6 from samples of powder, film, and photooxidized film. The broken lines are the calculated curves which will be discussed later. The evolution of $CH_3{-}Si{-}C_6H_5$ occurs mainly in a range of temperature from 550 to 750 K, centered near 660 K, which is consistent with the results[2,9] obtained from TGA. The film sample shows approximately a 20 K high-temperature shift as compared with the powder sample, suggesting a better heat resistance in the film state. The

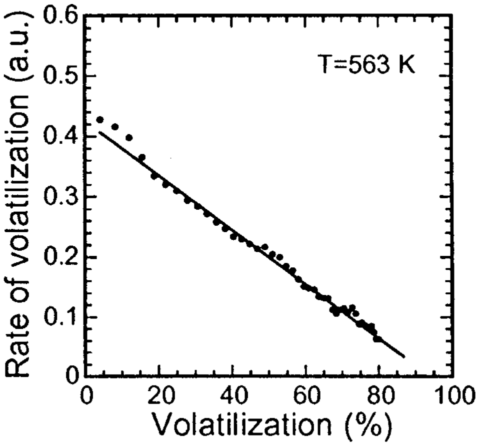

Figure 5. Rate of volatilization in the pyrolysis of PMPS at the temperature of 563 K.

photooxidized film has a broad peak with the shift to the highest temperature.

The evolution of C_6H_6 from the powder and film samples occurs mainly in a range of temperature from 550 to 750 K with a peak near 660 K, which almost simultaneously occurs with that of $CH_3-Si-C_6H_5$. It is noted that the evolution of C_6H_6 still continues above 800 K where the evolution of $CH_3-Si-C_6H_5$ nearly finishes. The effusion of benzene in high temperature indicates that the residues contain $Si-C_6H_5$ bonds but do not effuse $CH_3-Si-C_6H_5$. In the case of photooxidized film, the evolution of benzene starts from a lower temperature of 420 K and increases until above 800 K, which is quite different from that of the unoxidized film.

Kinetic Analysis

The thermal decomposition of PMPS is a type of depolymerization as mentioned above. Figure 5 shows the isothermal curve of the rate of volatilization of $CH_3-Si-C_6H_5$. The linear relation between the rate and the volatilization suggests that the decomposition reaction of PMPS is a first-order reaction. Many other experimental results also show that the depolymerization reaction is first-order.[11]

It is helpful to make a comparison between PMPS and poly-α-methylstyrene (PαMS), which has been well-studied on the basis of its thermal degradation, because the two kinds of polymers have similar points in molecular structure, both of them have the methyl and phenyl substituents. The reaction of thermal degradation of PαMS is found definitely to be first-order. The decomposition reaction is explained on the basis of a mechanism of random scissions of C−C bonds resulting in free radicals. This is followed by a rapid unzipping at the radical ends to give monomers.[12−14] Because the bond energy of Si−Si (~80 kcal/mol)[2] is smaller compared with that of C−C (~90 kcal/mol), it is most probable that the decomposition reaction in PMPS starts from the scission of Si−Si bond at a weak point in Si−Si backbone and the reaction of depolymerization occurs to effuse monomers from the end of the resulting radicals, having a similar process to that of PαMS. However, unlike PαMS having the alternating C−H bonds, PMPS contains no Si−H bonds in the main chains, thus the reaction of hydrogen transfer resulting in unsaturated end[14] is comparatively difficult to occur and therefore yields high monomer conversion. The rate of initial random scissions of Si−Si bonds is generally slower than that of unzipping and is therefore the rate-determining reaction. On the basis of the mechanism of thermal decomposition of PMPS, the reaction kinetic analysis is performed to obtain further information about the decomposition reactions.

It is clearly observed that three kinds of states of PMPS show different shapes of gas evolution spectra, suggesting that they have different activation energies of decomposition reactions.

The reaction kinetic analysis is a convenient method for the estimation of overall kinetic parameters. Various methods have been used to analyze the TGA or the differential thermal analysis (DTA) curves.[15−19] However, they could not be directly applied to the analysis of the evolution spectra obtained from mass spectrometer (MS). Here we review a kinetic model to analyze the pyrolysis of polymer detected by MS and from which the activation energies are deduced.

Let us consider that thermal decomposition occurs at an activation energy E and the volatile product is evolved to the vacuum, staying for a time τ to be detected by QMS in the chamber and then exhausted. The rate equation of the density of evolved product x in the chamber is written as

$$\mathrm{d}x/\mathrm{d}t = -x/\tau - \mathrm{d}x_\mathrm{p}/\mathrm{d}t \qquad (1)$$

where x_p is the density of radicals or units in molecules which contribute to the evolved product. In the steady state, $\mathrm{d}x/\mathrm{d}t = 0$, we have

$$x = -\tau\, \mathrm{d}x_\mathrm{p}/\mathrm{d}t \qquad (2)$$

Because

$$\mathrm{d}x_\mathrm{p}/dt = -x_\mathrm{p}{}^n K \qquad (3)$$

(where $K = A\exp(-E/RT)$ represents the rate constant and A is frequency factor which has the order of 10^{13}, n is the order of reaction, R and T are the gas constant and the absolute temperature, respectively), for the reaction of first-order, we have

$$x_\mathrm{p} = x_\mathrm{p0}\exp(-Kt)$$

where x_p0 is the original density of radicals or units in PMPS molecules; therefore

$$\mathrm{d}x_\mathrm{p}/\mathrm{d}t = -x_\mathrm{p0}K\exp(-Kt) \qquad (4)$$

From eq 2, we obtain the density of the evolved product written as

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$$x = x_{p0}\tau K \exp(-Kt) = x_{p0}\tau K \exp\left(-\int K\,dt\right) \quad (5)$$

Because the temperature is raised with a fixed rate α, $T = \alpha t$, dt is replaced by dT as d$T = \alpha$ dt, we then have

$$\begin{aligned} x &= x_{p0}\tau K \exp\left[-(1/\alpha)\int_0^T K\,dT\right] \\ &= x_{p0}\tau A \exp(-E/RT) \exp\left[-(A/\alpha)\int_0^T \exp(-E/RT)\,dT\right] \end{aligned} \quad (6)$$

This derivation is the same as that of the thermally stimulated conductivity (TSC)[20] which is used to investigate the defect levels in semiconductors. Equation 6 also has the same form as that derived by Ozawa using another method of kinetic analysis.[21]

The calculations using eq 6 do not fit well the experimental evolution spectra for C_6H_6 and $CH_3{-}Si{-}C_6H_5$, indicating that the premise of decomposition processes having constant activation energy may be unsuitable. Actually, Jellinek et al.[22] studied the thermal degradation of poly(methyl methacrylate) (PMMA) and pointed out that the activation energies depend not only on the chain length but also on the percentage of degradation, the activation energies are high at short chain and high percentage of degradation. Wall et al.[14] studied the pyrolysis of PαMS with different molecular weights and concluded that unlike the definite change in the activation energy for PMMA, no such a large change was found in the activation energy for depolymerization with increasing molecular weight in PαMS, but there still was a difference of more than 5 kcal per repeating unit. For PMPS, the decomposition reactions initiate at the weak points of Si−Si main chains, and it is reasonable to consider that the bond energies of weak Si−Si bonds would have a little difference caused by the initial distribution of molecular weights and distortion in molecules. In addition, during the heat treatment on PMPS, with an increase in the temperature, Si−Si main chains are gradually scissored and the weight loss increases. It indicates that PMPSs may have high activation energies of thermal decomposition at high temperature, in other words, a distribution of activation energies in PMPS molecules in pyrolysis are present. Assuming that it is a Gaussian distribution, the density of radicals and the units with an activation energy E in PMPS molecules $x_{p0}(E)$ can be written as

$$x_{p0}(\mathrm{E}) = x_{p0}\frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(E - E_{\max})^2}{2\sigma^2}\right] \quad (7)$$

where $E_{\max}$ is the activation energy at the distribution center and σ is the width of the distribution. The evolution of a gas at a temperature T is a sum of contribution of decomposition reactions with different activation energies. Therefore, eq 6 is rewritten as

$$x(T) = \int_0^\infty x_{p0}(E)\tau K(E) \exp\left[-(1/\alpha)\int_0^T K(E)\,dT\right]dE \quad (8)$$

The evolution spectra of $CH_3{-}Si{-}C_6H_5$ and C_6H_6 for PMPS in the states of powder, film, and photooxidized film are reconstructed using eq 8 with suitable values of $E_{\max}$ and σ.

Table 1. Theoretical Fitting Parameters for the Evolution Spectra of $(CH_3{-}Si{-}C_6H_5)^+$

state of PMPS	$E_{\max}$ (kcal/mol)	σ (kcal/mol)
powder	44.9	1.6
film	46.4	1.8
photooxidized film	46.8	2.4

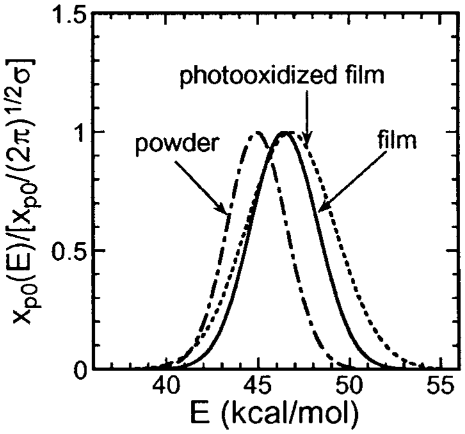

Figure 6. Distribution of activation energies of thermal decomposition in PMPS in the states of powder, film, and photooxidized film.

Table 2. Theoretical Fitting Parameters for the Evolution Spectra of Benzene

state of PMPS	fitting parameters (kcal/mol)					
	$E_{\max1}$	σ_1	$E_{\max2}$	σ_2	$E_{\max3}$	σ_3
powder			45.9	2.8	57.6	5.1
film			47.3	2.3	59.0	4.6
photooxidized film	36.9	3.5	46.1	3.7	58.1	3.2

Discussion

The calculated curves are plotted with broken lines in Figure 3 with experimental evolution spectra of the $CH_3{-}Si{-}C_6H_5$ fragment. The fitting parameters are listed in Table 1. The agreement between calculated curves and experimental spectra supports the validity of our model that the activation energies have a distribution. Figure 6 shows the distribution of activation energies used for the calculation. The distribution width of the activation energies in the powder and in the film sample is almost the same, but the energy at distribution center in the film sample is 1.6 kcal/mol larger than that in the powder sample. This suggests that there are stronger interactions among the PMPS molecules in film leading to the higher energy shift of the activation energies and hence the increasing of the decomposition temperature. The photooxidized PMPS film has a broad distribution of the activation energies with the distribution center shift to the highest energy, which might be due to the shortening of PMPS molecules and the different molecular weights. The effect of the stable Si−O structures also plays an important role in increasing of the activation energies.

The evolution of the phenyl substituents is analyzed by the same manner as that of $CH_3{-}Si{-}C_6H_5$. Calculated curves for benzene from PMPS in the states of powder, film, and photooxidized film are plotted with

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broken lines in Figure 4. The fitting parameters are listed in Table 2. The evolution spectra of benzene are well explained with two steps of decomposition in the powder and thin film samples and with three steps in the photooxidized film. The values of $E_{\max}$ of the powder and film samples in the first step are 45.9 and 47.3 kcal/mol, which are almost consistent with that in the evolution of $CH_3-Si-C_6H_5$. It suggests that the evolved benzene in the first step is due to the disconnection of phenyl radical from Si accompanied with the decomposition reactions of Si–Si main chains. The activation energies of the second step above 800 K are about 11.7 kcal/mol higher than that of the first step, corresponding mainly to the reactions of the random cleavages of $Si-C_6H_5$ bonds contained in the residues. Beside these two steps, there is a lower temperature evolution step with activation energies near 36.9 kcal/mol in the photooxidized film, in which the evolved benzene is considered to be from phenyl radical containing products where some weak bonds, produced by UV irradiation, are present. The strong evolution of benzene from the photooxidized film in the high-temperature step above 750 K might indicate that there are residues of Si–O containing substances in which phenyl radicals are bonded.

Conclusion

Pyrolysis of PMPS in the states of powder, film, and photooxidized film has been analyzed with the use of QMS. The mechanism of thermal decomposition of PMPS is very similar to that of PαMS, which is that the random initiation results in the formation of free-radical ends and then proceeds to unzip into monomers. Three kinds of states of PMPS have different activation energies of decomposition reactions. The analysis of the evolution spectra based on the activation energies with a Gaussian distribution self-consistently gives information on the activation energies of decomposition of the Si–Si main chains and $Si-C_6H_5$ bonds in PMPS molecules. Because of the difference in the interaction among PMPS molecules, the film sample has higher decomposition activation energies and hence higher heat resistance than the powder sample. For the photooxidized film, the shifting to the highest energy and the broadening of the distribution of activation energies are considered to be due to the shortening of PMPS molecules and the different molecular weights as well as the effect of the Si–O structures. The evolution of phenyl substituents has two different processes for the unoxidized polysilane and three processes for the photooxidized polysilane, one of the processes for both the unoxidized and photooxidized polysilanes corresponds with the evolution of the units of the polysilane $CH_3-Si-C_6H_5$. The more intense evolution of phenyl substituents in the high-temperature region for the photooxidized polysilane than for the unoxidized polysilane suggests that structures containing Si–O bonds make the Si–phenyl bonds strong.

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