

# Infrared Spectroscopic Study of SiO<sub>x</sub> Film Formation and Decomposition of Vinyl Silane Derivative by Heat Treatment. I. On KBr and Gold Surface

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**ABSTRACT:** The free-radical copolymerization of vinyltrimethoxysilane (VTS) with vinylimidazole (VI) was carried out in benzene at 68°C. Thermooxidative degradation and the SiO<sub>x</sub> film-formation mechanism of poly(VI-co-VTS) both on gold and KBr were studied with Fourier transform infrared (FTIR) spectroscopy. Reflection-absorption (R-A) spectra on gold were compared with transmission spectra on KBr. In the initial stage of heat treatment, the Si—O—Si bond formation was caused mainly by the residual water in the copolymer film. As heating time increased, however, both the water resulting from the thermal decomposition of the copolymer and the water vapor in air began to participate in the hydrolysis of the Si—O—CH<sub>3</sub> group followed by the condensation reaction. The structure of the SiO<sub>x</sub> film became closer to the structure of SiO<sub>2</sub> with increasing heating temperature. In addition, the differences between the transmission spectra and R-A spectra were observed at the peaks related to Si—O—Si stretching due to the optical effect. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 775–784, 1998

**Key words:** poly(VI-co-VTS), thermooxidative degradation; amorphous SiO<sub>x</sub> film

## INTRODUCTION

Silane derivatives have been widely used in many ways such as in primers, coupling agents, electronic insulators, and corrosion inhibitors.<sup>1–10</sup> Especially, their applications at high temperature have attracted much attention in various fields due to their good thermal stability. Silane derivatives with siloxane linkages have good thermal properties in comparison with other organic compounds due to their inorganic property. Inorganic properties of silane derivatives are caused by the siloxane network structure formation.

For corrosion protection on the copper surface, silane-modified polyvinylimidazole (PVI) suppressed copper corrosion at a higher temperature

than did organic corrosion inhibitors.<sup>7–9</sup> They could protect the copper surface from corrosion above 360°C in air because they formed protective inorganic SiO<sub>x</sub> film on the copper surface through the formation of the infinite siloxane network structure. Some researchers studied the thermal degradation of PVI both on KBr and on copper to better understand the corrosion inhibition mechanism of PVI on copper.<sup>11,12</sup> However, the SiO<sub>x</sub> film formation from silane-modified PVI has not been extensively studied even though this SiO<sub>x</sub> film formation is a very important factor in corrosion protection on metal both in humid conditions and at elevated temperature.<sup>7–10</sup> Therefore, we shall investigate the thermooxidative degradation of silane-modified PVI, which is related to SiO<sub>x</sub> film formation.

In this study, a vinyl silane-modified imidazole copolymer was synthesized by free-radical copolymerization. The SiO<sub>x</sub> film-formation mechanisms

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on gold and KBr as the inert substrates were investigated by FTIR with the variation of heat treatment. The spectra taken on gold and KBr were analyzed for understanding the thermal decomposition and crosslinking mechanism of the silane-modified imidazole copolymer.

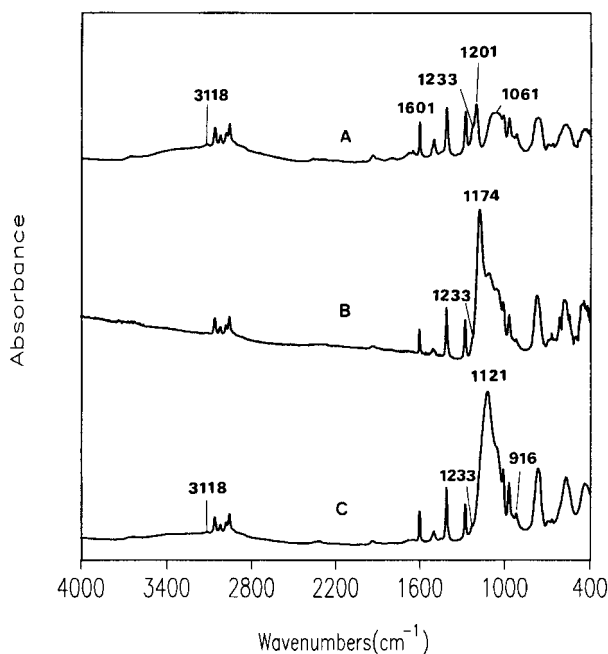
## EXPERIMENTAL

Vinylimidazole (VI) was purchased from Aldrich Chemical Co., and vinyltrimethoxysilane (VTS), from Petrarch Systems Inc. They were distilled *in vacuo* to yield pure and colorless liquids. Azobisisobutyronitrile (AIBN) from Wako Pure Chemical Industries, Ltd., was dissolved in warm methanol (35°C), recrystallized in an ice bath, and then dried in a vacuum oven at room temperature for 2 days. Poly(VI-co-VTS) was synthesized by free-radical copolymerization using AIBN as an initiator. VI and VTS were copolymerized in benzene at 68°C with stirring in an argon atmosphere. The mol ratio of VI to VTS in the feed was 3 : 7. The total monomer concentration was 2M, and the initiator concentration was fixed at  $2 \times 10^{-3}$  M.

The copolymer solution was cast both onto a KBr plate and a gold surface with a microsyringe and the samples were dried at 60°C for 12 h in air before testing to remove the solvent in the polymer film. Film thickness was controlled with the variation of the copolymer concentration and calculated based on the concentration of the copolymer solution, copolymer density, and the area of the substrate.

FTIR reflection-absorption (R-A) spectroscopy was used to monitor the thermal degradative crosslinking of poly(VI-co-VTS) coated on gold. The spectrometer was continuously purged with nitrogen gas to remove the water vapor and atmospheric CO<sub>2</sub>. Absorbance spectra were obtained using a Bomem MB-100 spectrometer at a resolution of 4 cm<sup>-1</sup> and 32 scans were collected. A Graseby Specac P/N 19650 monolayer/grazing angle accessory was used. The angle of incidence was 78° and a freshly cleaned gold surface was used to obtain the reference spectrum. In addition, the thermal behaviors of the copolymer on the KBr plate were monitored with FTIR transmission spectroscopy.

Copolymer-coated samples were heated at 360°C to study the thermal degradation mechanism of the copolymer. Each sample was heated for 1 min at 360°C in air and then characterized by FTIR. This process was repeated on the same



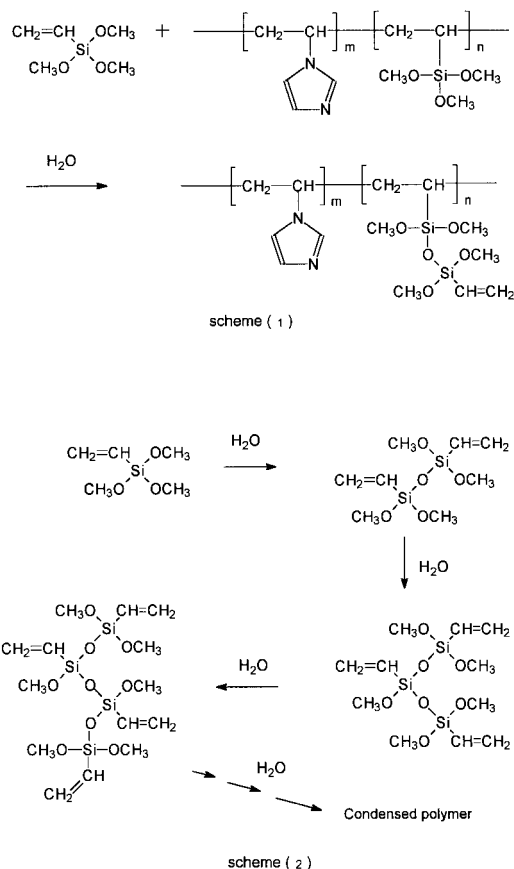
**Figure 1** FTIR spectra of the copolymer before heat treatment: (A) R-A spectrum of thick (2  $\mu\text{m}$ )-coated sample (on gold); (B) R-A spectrum of thin (0.6  $\mu\text{m}$ )-coated sample (on gold); (C) transmission spectrum on KBr (0.6  $\mu\text{m}$ ).

sample with a 1-min increment in heating time until the heat treatment time reached 9 min.

## RESULTS AND DISCUSSION

The thermal degradation mechanism of poly(VI-co-VTS), which is related to the SiO<sub>x</sub> film formation, was studied both on gold and KBr. Figure 1 shows two R-A spectra of the copolymers with the different coating thicknesses on gold and one transmission spectrum on KBr.

There are a few differences in spectra A and B due to the optical distortion. The CH rocking peak from the Si—O—CH<sub>3</sub> group is quite different in the two spectra. In spectrum B, the CH rocking peak appears at 1174 cm<sup>-1</sup> due to the overlapping of two peaks at 1194 and 1151 cm<sup>-1</sup>. The former is due to the CH rocking from the Si—O—CH<sub>3</sub> group, and the latter is attributed to that from the Si—O—CH<sub>2</sub>CH<sub>3</sub> group.<sup>13,14</sup> The existence of the Si—O—CH<sub>2</sub>CH<sub>3</sub> group results from the alcoholic exchange reaction by ethanol used as a solvent. However, the CH rocking mode in spectrum A appears at 1201 cm<sup>-1</sup>. This is ascribed to the shift of the peak at 1194 cm<sup>-1</sup> by the effect of the



**Figure 2** Scheme of the copolymer film formation on gold or on KBr.

shoulder peak at  $1233\text{ cm}^{-1}$ . The peak at  $1233\text{ cm}^{-1}$  is designated as the ring vibration of VI.<sup>11</sup> The peak at  $1151\text{ cm}^{-1}$  is overlapped by other peaks around  $1061\text{ cm}^{-1}$ . The peak at  $3118\text{ cm}^{-1}$  corresponds to the  $=\text{C}-\text{H}$  stretching mode parallel to the imidazole ring plane of VI.<sup>11</sup> There are also a few differences between spectra B and C with the same coating thickness due to the optical effect on the nontransmission spectra. The strong  $\text{C}-\text{H}$  rocking peak at  $1121\text{ cm}^{-1}$  in spectrum C is different from that on gold in its position.

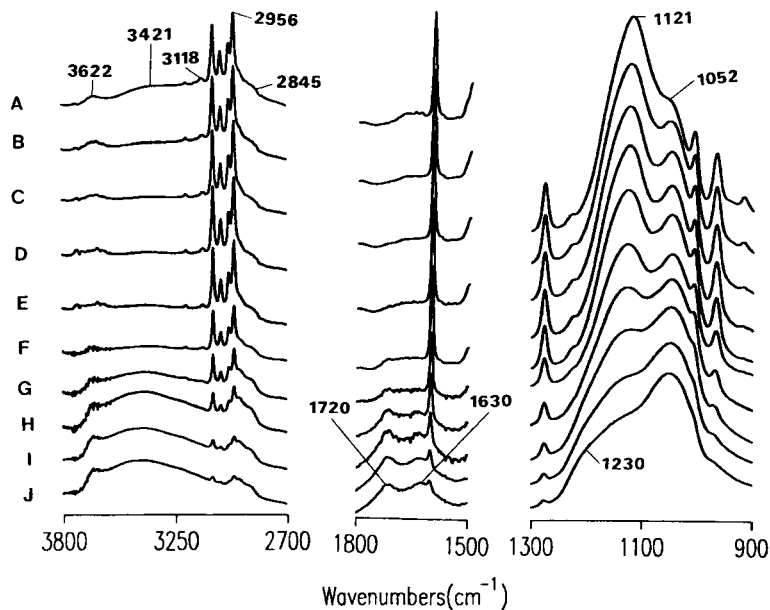
The peak at  $1601\text{ cm}^{-1}$  in all spectra is due to the  $\text{C}=\text{C}$  stretching mode from the VTS monomer. As expected from the relative reactivity ratios of the two monomers,<sup>15</sup> the existence of this peak confirms that the VTS monomer remains in the copolymerization system in spite of enough reaction time. Unreacted VTS exists in the polymer film through the  $\text{Si}-\text{O}-\text{Si}$  bond formation because it can undergo the condensation reaction with the VTS unit in the copolymer chain [scheme (1) in Fig. 2]. In addition, VTS can form the polymeric film through the  $\text{Si}-\text{O}-\text{Si}$  bond formation

among VTS monomers [scheme (2) in Fig. 2]. These reactions are catalyzed by the water in the air during the drying process. These postulated schemes are sketched in Figure 2.

### On KBr

The thermal degradation and  $\text{SiO}_x$  film-formation mechanism of the copolymer on KBr were investigated. Figure 3 shows the changes in the transmission spectra of the copolymer on KBr as a function of heating time. Heating temperature was fixed at  $360^\circ\text{C}$ . In Figure 3(A), the peak at  $3622\text{ cm}^{-1}$  is assigned to the  $\text{O}-\text{H}$  stretching of the nonhydrogen-bonded  $\text{Si}-\text{OH}$  group, and the broad band around  $3421\text{ cm}^{-1}$  is due to the water hydrogen-bonded to the imidazole ring and the hydrogen-bonded  $\text{Si}-\text{OH}$ . These peaks indicate that the water vapor is absorbed in the copolymer film due to the hygroscopic property of VI and that it changes the  $\text{Si}-\text{O}-\text{CH}_3$  group into the  $\text{Si}-\text{OH}$  group by partial hydrolysis during film formation. The shoulder peak at  $1052\text{ cm}^{-1}$  in Figure 3(A) is assigned to the  $\text{Si}-\text{O}-\text{Si}$  stretching peak, which means that some hydrolyzed  $\text{Si}-\text{OH}$  groups are condensed to form the  $\text{Si}-\text{O}-\text{Si}$  linkage during film formation. As heating time increases, the peak around  $3421\text{ cm}^{-1}$  and the peak at  $1121\text{ cm}^{-1}$  are reduced in intensity. However, the peak at  $3622\text{ cm}^{-1}$  is hardly changed in intensity, and the peak at  $1052\text{ cm}^{-1}$  increases in intensity. These facts suggest that the residual water in the copolymer film vaporizes during heat treatment to induce the hydrolysis of the  $\text{Si}-\text{O}-\text{CH}_3$  groups followed by the condensation reaction among the hydrolyzed  $\text{Si}-\text{OH}$  groups. Accordingly, the peak intensity at  $1052\text{ cm}^{-1}$  ( $\text{Si}-\text{O}-\text{Si}$  stretching) increases and the peak intensity at  $1121\text{ cm}^{-1}$  ( $\text{Si}-\text{O}-\text{C}$  stretching) decreases gradually as heating time increases [Fig. 3(B-E)].

On the other hand, the bands due to the polar oxidative products (e.g.,  $1720$  and  $1630\text{ cm}^{-1}$ ) by thermal degradation of the copolymer are hardly observed in Figure 3(B-D), which begin to appear around  $1720\text{ cm}^{-1}$  in Figure 3(E). As heating time is increased, the intensities of these peaks increase up to 6 min and then are hardly changed in spite of more reduction of the copolymer peak. This suggests that the oxidation products were consumed by the thermal decomposition. The copolymer peaks decrease continuously with increasing heating time due to thermal oxidation followed by decomposition. The peak at  $3118\text{ cm}^{-1}$  from the VI unit is not observed any more at 8



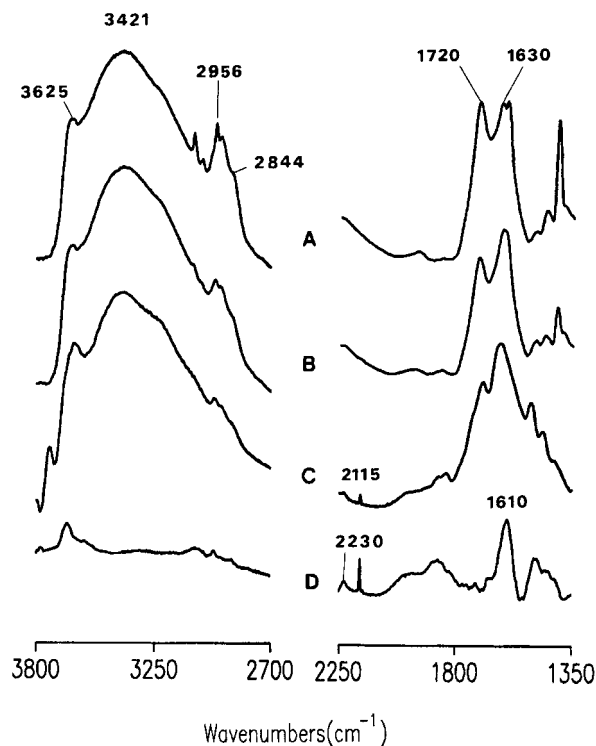
**Figure 3** FTIR transmission spectra of the copolymer film on KBr as a function of heating time at 360°C: (A) control; (B) 1 min; (C) 2 min; (D) 3 min; (E) 4 min; (F) 5 min; (G) 6 min; (H) 7 min; (I) 8 min; (J) 9 min.

min of heating time, but the peaks from the VTS unit are still observed at 9 min of heating time.

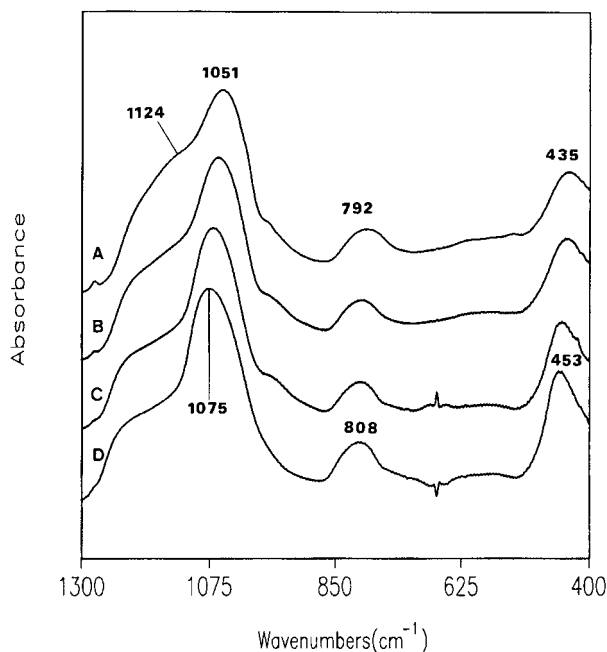
In Figure 3(F–J), the peak intensities at 3622, 3421, and 1052  $\text{cm}^{-1}$  increase as heating time is increased. The new shoulder peak appears at 1230  $\text{cm}^{-1}$  in Figure 3(J). These suggest that water is introduced into the copolymer film to induce the hydrolysis of the Si–O–CH<sub>3</sub> group and the condensation reaction among the Si–OH groups. The water introduced into the copolymer film can be explained by two mechanisms: One is associated with H<sub>2</sub>O formation by the thermal decomposition of the copolymer. The other is related to the water absorption of water vapor in air.

From these results, it can be concluded that the Si–O–Si bond formation during heat treatment (4–9 min) is due to the adsorption of the water vapor in air as well as the water formation by the thermal decomposition of the copolymer. However, all the Si–O–CH<sub>3</sub> groups have not been converted into Si–OH and Si–O–Si groups, and the peaks from the Si–O–CH<sub>3</sub> are still observed at 2956 and 2845  $\text{cm}^{-1}$ .

For further thermal crosslinking, the sample was heated at higher temperature. Figures 4 and 5 show the transmission spectra of the copolymer on KBr with increasing heating temperature. In Figure 4, the peaks from the double bond of VTS decrease to disappear at 400°C due to the enhanced thermal oxidation as heating temperature



**Figure 4** FTIR transmission spectra of the copolymer film on KBr heated in air with increasing heating temperature: (A) for 9 min at 360°C; (B) for 15 min at 360°C; (C) for 15 min at 400°C; (D) for 15 min at 500°C.



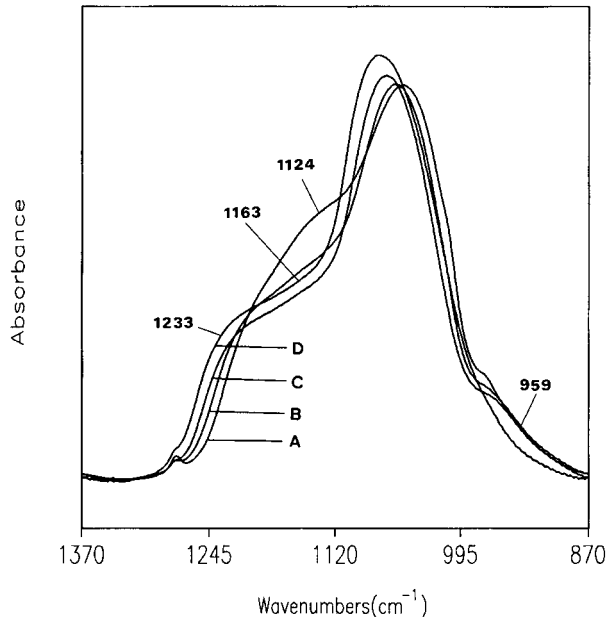
**Figure 5** FTIR transmission spectra (1300–400  $\text{cm}^{-1}$ ) of the copolymer film on KBr heated in air with increasing heating temperature: (A) for 9 min at 360°C; (B) for 15 min at 360°C; (C) for 15 min at 400°C; (D) for 15 min at 500°C.

increases. The 1720 and 1610  $\text{cm}^{-1}$  peaks decrease in intensity with heating temperature due to the thermal decomposition and disappear at 500°C. The 1610  $\text{cm}^{-1}$  peak at 500°C is ascribed to the bending peak from residual water trapped in the silica structure.<sup>16</sup> The peak at 2230  $\text{cm}^{-1}$ , which appears first at 400°C, is due to the CN group from the thermal decomposition of the VI ring.<sup>13</sup> The peak at 2115  $\text{cm}^{-1}$  is attributed to the formation of KCN.<sup>13</sup> The broad band around 3421  $\text{cm}^{-1}$  from residual water is drastically reduced at 500°C. The 2956 and 2844  $\text{cm}^{-1}$  peaks from Si—OCH<sub>3</sub> also decrease with heating temperature and disappear at 500°C. This means that the continuous hydrolysis followed by the condensation reaction proceeds by the enhanced heat treatment. The peak at 3625  $\text{cm}^{-1}$  is observed even after heat treatment at 500°C. Some Si—OH groups remain without the Si—O—Si bond formation in the siloxane network structure. The existence of the Si—OH groups is attributed to the geometric hindrance.

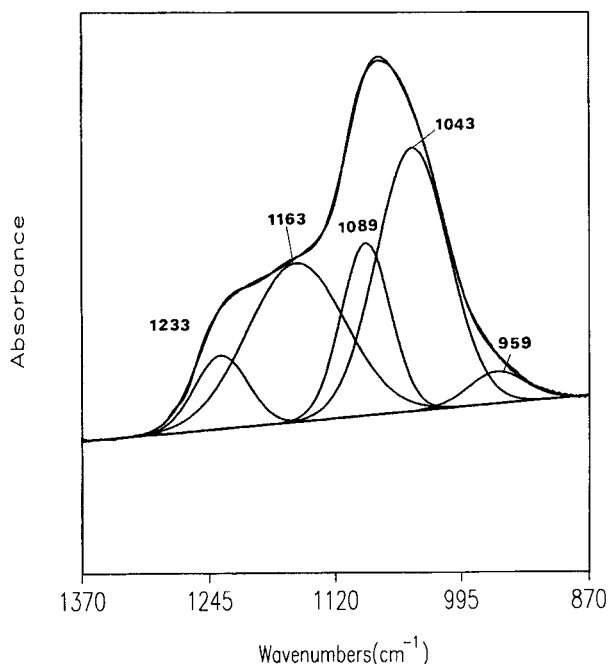
Figure 5 demonstrates the changes of the peaks related to Si—O—Si linkage as a function of heating temperature. As heating temperature increases, the Si—O—C peak intensity at 1124  $\text{cm}^{-1}$  is reduced. The in-phase Si—O—Si stretch-

ing peak shifts from 1051 to 1075  $\text{cm}^{-1}$ ; the Si—O—Si bending, from 792 to 808  $\text{cm}^{-1}$ ; and the Si—O—Si rocking, from 435 to 453  $\text{cm}^{-1}$ . These shifts suggest that the siloxane network structure approaches the structure of stoichiometric SiO<sub>2</sub> as heating temperature increases. It was reported that as the in-phase Si—O—Si stretching frequency is shifted to higher frequency  $x$  becomes closer to 2 in the SiO<sub>x</sub> amorphous film.<sup>17–21</sup>

The 1370–870  $\text{cm}^{-1}$  region of the spectra in Figure 6 was closely investigated. As heating temperature increases, the shoulder peak at 1233  $\text{cm}^{-1}$ , which is assigned to the out-of-phase Si—O—Si stretching,<sup>22</sup> is intensified and shifted to higher frequency. This shoulder peak appears when four oxygens are bonded to each silicon atom. This shift is attributed to the increase of the four-bridged Si atom. Therefore, as the fraction of stoichiometric SiO<sub>2</sub> increases in the SiO<sub>x</sub> film ( $x < 2$ ), the shoulder peak at 1233  $\text{cm}^{-1}$  is intensified and shifted to higher frequency due to the increased stoichiometric SiO<sub>2</sub>. This is supported by the fact that the peak from in-phase Si—O—Si stretching is shifted to a higher frequency. This increase in the SiO<sub>2</sub> fraction is accompanied by the reduction in Si—O—C (1124  $\text{cm}^{-1}$ ) and Si—OH peak (959  $\text{cm}^{-1}$ ). However, at 500°C, the peak intensity around 1163  $\text{cm}^{-1}$  increases to the



**Figure 6** FTIR transmission spectra (1370–870  $\text{cm}^{-1}$ ) of the copolymer film on KBr heated in air with increasing heating temperature: (A) for 9 min at 360°C; (B) for 15 min at 360°C; (C) for 15 min at 400°C; (D) for 15 min at 500°C.



**Figure 7** Curve-fitted spectrum of Figure 6(D).

contrary. Since the Si—O—C group is no longer at 500°C (Fig. 4), the peak at 1163  $\text{cm}^{-1}$  can be assigned to the Si—O—Si from the  $\text{RSiO}_{1.5}$  structure.<sup>23–26</sup> From these results, the peaks in Figure 6(D) can be resolved into five different peaks. Figure 7 shows the curve-fitted spectrum of Figure 6(D). Each peak is assigned in Table I.

The effect of the film thickness on the  $\text{SiO}_x$  film formation on KBr was investigated. Table II represents the peak shifts of the copolymers with different coating thicknesses as a function of heating temperature. The peak shifts depend on the heating temperature, not on the coating thickness in this experimental condition. It was reported that as coating thickness increases the residual stress in the film increases and the peak is shifted to lower frequency.<sup>1,27,28</sup> However, the effect of the coating thickness on the frequency shift is negligible. Therefore, the higher shifts of the peaks re-

lated to the Si—O—Si linkage are due mainly to the increase of the  $\text{SiO}_2$  fraction with increasing heating temperature.<sup>17–21</sup>

### On Gold

Compared with the transmission spectra of the copolymer film on KBr, R-A spectra on gold show some spectral differences. The spectral changes of the thin-coated copolymer film on gold with increasing heating time at 360°C are demonstrated in Figure 8. As heating time increases, the peak at 1105  $\text{cm}^{-1}$  (Si—O—C stretching) decreases. The peak at 1176  $\text{cm}^{-1}$  decreases to become broader, showing a higher shift. The peak at 1052  $\text{cm}^{-1}$  (Si—O—Si stretching) increases to become broad. These indicate that Si—O—C is hydrolyzed and condensed to form Si—O—Si linkage as heating time increases. However, the peak intensity and the peak shape are different from the transmission spectra due to the optical effect.

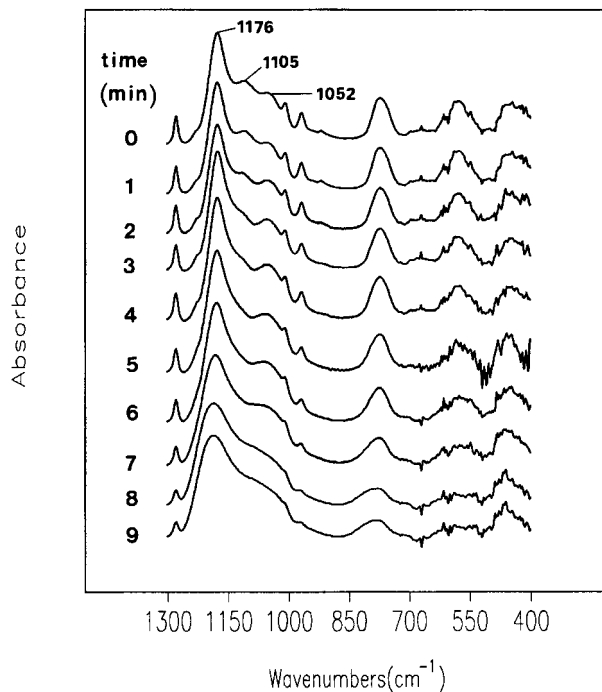
To investigate the thermooxidative degradation of the copolymer followed by  $\text{SiO}_x$  film formation at higher temperature, the sample was heated with increasing temperature. Figures 9 and 10 show the R-A spectra of the copolymer as a function of heating temperature. Judging from the disappearance of the peaks in spectrum 9(B), the hydrolysis of the Si—O— $\text{CH}_3$  group and the oxidation of the copolymer are considered to be nearly completed. The broad water peak (3421  $\text{cm}^{-1}$ ) and the bands due to the oxidative products (1720 and 1630  $\text{cm}^{-1}$ ) are reduced in intensity with increasing heating temperature, and only small peaks are observed at 500°C. Figure 10(B) shows two peaks at 1239 and 1061  $\text{cm}^{-1}$  with a shoulder peak at 1185  $\text{cm}^{-1}$ . This shoulder peak is attributed to the Si—O—Si stretching of  $\text{RSiO}_{1.5}$  with the structure of the condensed polysilsesquioxane. The existence of the two peaks at 1185 and 1061  $\text{cm}^{-1}$  suggest that polysilsesquioxane is an ordered ladder polymer.<sup>26</sup> The drastic change in

**Table I** Peak Positions of  $\text{SiO}_x$  Film on KBr After Heat Treatment at 500°C

Peak Positions ( $\text{cm}^{-1}$ )	Assignments
1233	Out-of-phase Si—O—Si stretching from $\text{SiO}_2$
1163	Si—O—Si stretching from $\text{RSiO}_{1.5}$
1089	In-phase Si—O—Si stretching from $\text{SiO}_2$
1043	Si—O—Si stretching from $\text{RSiO}_{1.5}$
959	Si—O stretching from Si—OH

**Table II** Peak Positions of the SiO<sub>x</sub> Film With Different Coating Thickness

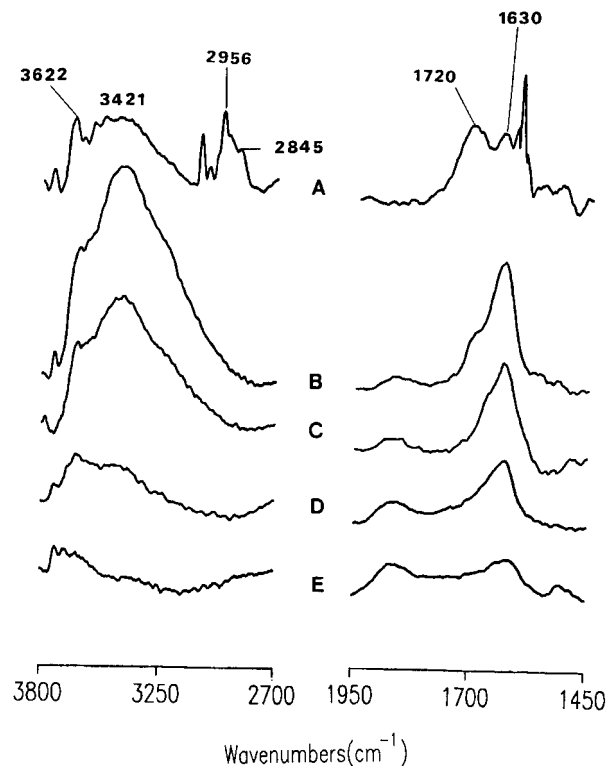
Thickness (μm)	360°C for 9 min (cm <sup>-1</sup> )			360°C for 15 min (cm <sup>-1</sup> )			400°C for 15 min (cm <sup>-1</sup> )			500°C for 15 min (cm <sup>-1</sup> )		
	Stretching	Bending	Rocking	Stretching	Bending	Rocking	Stretching	Bending	Rocking	Stretching	Bending	Rocking
2	1052	793	437	1061	803	441	1069	807	448	1077	808	454
1	1051	792	436	1059	803	441	1068	803	447	1075	808	453
0.6	1050	784	435	1058	802	441	1069	803	447	1077	803	454
0.4	1051	785	437	1060	797	441	1069	803	448	1077	807	454
0.2	1050	784	436	1060	797	442	1070	802	448	1077	808	454



**Figure 8** FTIR R-A spectra (1300–400 cm<sup>-1</sup>) of the copolymer film on gold with increasing heating time at 360°C.

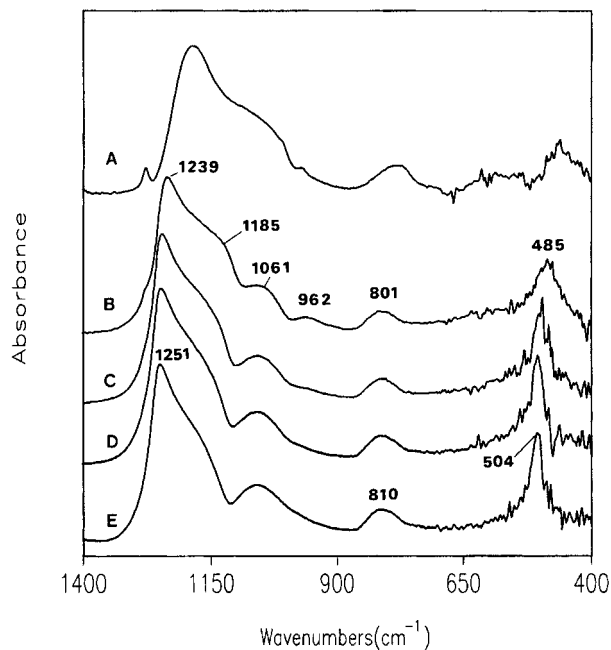
spectrum 10(B) is due to the disappearance of the Si—OCH<sub>3</sub> groups, which are converted into the Si—OH group or Si—O—Si linkage. This explanation is supported by the extinction of the Si—O—C peaks at 2956 and 2845 cm<sup>-1</sup> in Figure 9(B). As heating temperature increases, the peak at 1239 cm<sup>-1</sup> is shifted to 1251 cm<sup>-1</sup>. The peak at 801 cm<sup>-1</sup> (Si—O—Si bending) is shifted to 810 cm<sup>-1</sup>, and the peak at 485 cm<sup>-1</sup> (Si—O—Si rocking), to 504 cm<sup>-1</sup>. These shifts are observed in the transmission spectra (Fig. 5) even though the degree of shift is different. These shifts can be explained in the same way as for the transmission spectra. In addition, as heating temperature increases, the peak at 962 cm<sup>-1</sup> decreases gradually. It is related to the Si—OH group, and the reduction in this peak suggests that the condensation between the Si—OH groups proceeds with increasing heating temperature.

The 1370–870 cm<sup>-1</sup> region in Figure 10 is demonstrated in Figure 11. As heating temperature increases, the peak at 1239 cm<sup>-1</sup> is shifted to 1251 cm<sup>-1</sup> and its peak height increases. However, the shoulder peak at 1185 cm<sup>-1</sup> from RSiO<sub>1.5</sub> is reduced in intensity with increasing heating temperature.<sup>29</sup> This suggests that RSiO<sub>1.5</sub> is converted into SiO<sub>2</sub>. On the other hand, the shift in the in-

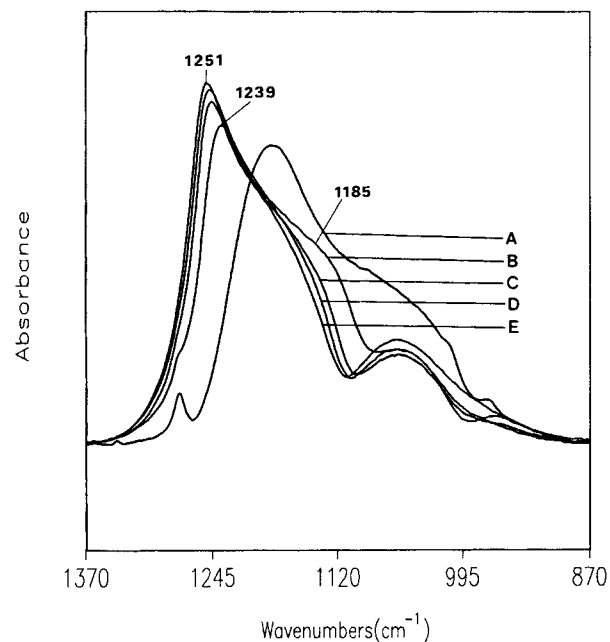


**Figure 9** FTIR R-A spectra of the copolymer film on gold heated in air with increasing heating temperature: (A) for 9 min at 360°C; (B) for 15 min at 360°C; (C) for 15 min at 420°C; (D) for 15 min at 460°C; (E) for 15 min at 500°C.

phase Si—O—Si stretching is not distinct in the R-A spectra due to the optical effect. The remarkable differences between the transmission and R-A spectra are observed in the 1370–870  $\text{cm}^{-1}$  region. In transmission spectra (Fig. 7), the transmission spectra resulting from heating at 500°C show the high intensity at 1075  $\text{cm}^{-1}$  with a shoulder peak at 1233  $\text{cm}^{-1}$ . In the R-A spectra, the reverse is observed. The structures of  $\text{SiO}_x$  film in both cases are expected to be similar because the orientation of the copolymer on gold and KBr is the same. Consequently, this spectral difference is thought to be caused by the optical effect. The longitudinal optical (LO) mode to the surface is stronger in the R-A spectrum due to the sensitivity of R-A spectroscopy to the LO mode. To the contrary, the transverse optical (TO) mode is weaker in the R-A spectrum. These facts support that the peak at 1233  $\text{cm}^{-1}$  (transmission spectra) and the peak at 1251  $\text{cm}^{-1}$  (R-A spectra) are due to the out-of-phase Si—O—Si stretching and that the peak at 1089  $\text{cm}^{-1}$  (transmission spectra) and the peak at 1075  $\text{cm}^{-1}$  (R-A spectra) are assigned



**Figure 10** FTIR R-A spectra (1400–400  $\text{cm}^{-1}$ ) of the copolymer film on gold heated in air with increasing heating temperature: (A) for 9 min at 360°C; (B) for 15 min at 360°C; (C) for 15 min at 420°C; (D) for 15 min at 460°C; (E) for 15 min at 500°C.



**Figure 11** FTIR R-A spectra (1370–870  $\text{cm}^{-1}$ ) of the copolymer film on gold heated in air with increasing heating temperature: (A) for 9 min at 360°C; (B) for 15 min at 360°C; (C) for 15 min at 420°C; (D) for 15 min at 460°C; (E) for 15 min at 500°C.

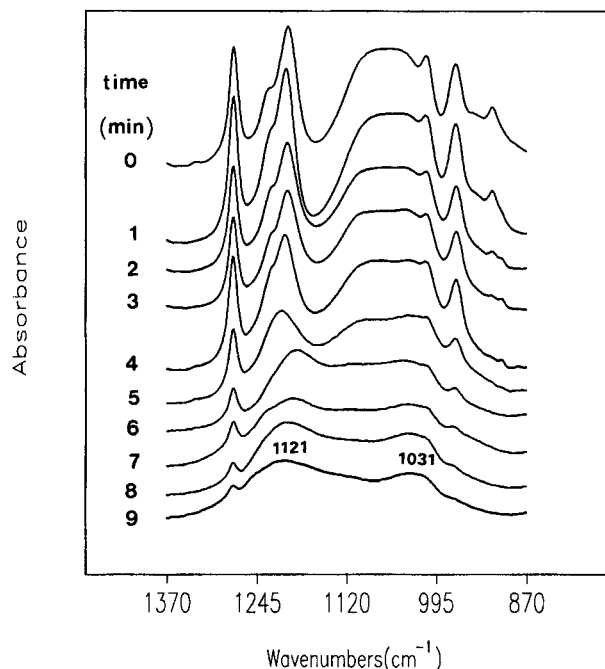


to the in-phase Si—O—Si stretching. In addition, the peak at 1194 cm<sup>-1</sup> (R-A spectra) is stronger than the shoulder peak at 1163 cm<sup>-1</sup> (transmission spectra). These Si—O—Si stretching peaks from the R-SiO<sub>1.5</sub> unit become weaker in intensity with increasing heating temperature due to the conversion into the SiO<sub>2</sub> structure.

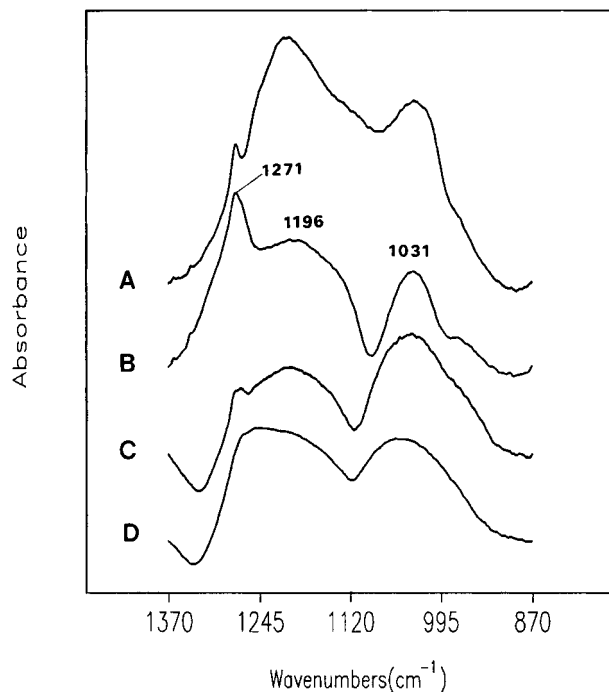
In contrast to the transmission spectra, the thick-coated sample has some spectral differences from the thin-coated sample in the R-A spectra. Their spectral changes are shown in Figures 12 and 13. Especially, the peaks in the 1370–870 cm<sup>-1</sup> region are quite different in positions and in intensity. In Figure 13, the in-phase Si—O—Si stretching peak at 1031 cm<sup>-1</sup> is stronger and broader than in Figure 10 because the relative peak intensity from the TO mode increases with increasing coating thickness. The out-of-phase Si—O—Si stretching peak appears at 1271 cm<sup>-1</sup>, showing a higher shift. This is due to the optical effect, which is observed at the oblique incidence angle.<sup>22</sup>

## CONCLUSIONS

The SiO<sub>x</sub> film both on KBr and gold was formed by thermal heating, and the thermal degradation



**Figure 12** FTIR R-A spectra (1370–870 cm<sup>-1</sup>) of the thick (2 μm)-coated copolymer film on gold with increasing heating time at 360°C.



**Figure 13** FTIR R-A spectra of the thick (2 μm)-coated copolymer film on gold heated in air with increasing heating temperature: (A) for 9 min at 360°C; (B) for 15 min at 420°C; (C) for 15 min at 460°C; (D) for 15 min at 500°C.

and crosslinking mechanism of poly(VI-co-VTS) was investigated with FTIR. In the initial stage of heat treatment, the Si—O—Si bond formation was caused mainly by the residual water in the copolymer film and the water vapor in air. However, as heating time increased, the water resulting from thermal decomposition of the copolymer began to participate in the crosslinking reaction. The structure of the SiO<sub>x</sub> film formed by thermal heating becomes closer to the structure of SiO<sub>2</sub> as heating temperature increases, but the stoichiometric SiO<sub>2</sub> film was not formed. The SiO<sub>x</sub> film after heating at 500°C is composed mainly of SiO<sub>2</sub> and RSiO<sub>1.5</sub>. Although the final structures of the SiO<sub>x</sub> film are similar both on KBr and gold, they showed the spectral differences in the 1370–870 cm<sup>-1</sup> region due to the optical effect. The spectral changes with coating thickness are observed in the R-A spectra due to the optical effect, but not in the transmission spectra.

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