

# Preparation of $\text{CH}_3\text{SiO}_{3/2}$ Gel Film on Aqueous Solutions. Infrared Spectroscopic Study of the Reaction in the Gel Film

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An oligomer solution was prepared from methyltriethoxysilane.  $\text{CH}_3\text{SiO}_{3/2}$  gel film was prepared by pouring the oligomer solution onto an aqueous solution. To improve this preparation method, the supporting solution was substituted by aqueous ammonia solutions after gelation. The structure of these films was investigated by FTIR attenuated total reflectance (ATR). This treatment shortened the time for the oligomer solution to become rigid on the supporting solution and caused a decrease of the number of Si–OH bonds in the gel film. The results are discussed based on the mechanism of condensation reaction in the film.

## Introduction

Inorganic gel films can be used as microfilters or membranes for gas separations,<sup>1</sup> which are usually supported on macroporous substrates. Several attempts have been made to prepare thick self-sustained gel films by sol–gel processes.<sup>2–4</sup> These films could be transformed to thin glass films. Yamane et al. prepared thick  $\text{SiO}_2$  gel films at the interface of a silicon alkoxide containing solution and an aqueous solution by using various hydrolysis catalysts.<sup>2</sup> Sakka scooped silica gel films from an oligomer solution, which was prepared from silicon alkoxide at a low ratio of  $\text{H}_2\text{O}/\text{Si}$ .<sup>3</sup> Recently, a  $\text{CH}_3\text{SiO}_{3/2}$  gel film was prepared by pouring an alkoxide-derived oligomer solution on an aqueous solution having a higher density than the oligomer solution.<sup>4</sup> It was found that both the immiscibility of the reaction product in the supporting solution and the interface energy changed with the degree of polymerization of siloxane. Transparent gel films could be obtained easily by controlling the interface energy, which varied with the alcohol content of the supporting solution. The film remained very sticky, however, after gelation and had to be kept on the supporting solution for more complete reaction until it became possible to scoop the film. Also, the concentration of Si–OH bonds remained high in the gel film, making the film reactive. In this study,  $\text{CH}_3\text{SiO}_{3/2}$  gel film was prepared by using the method shown in ref 4. The supporting solution was substituted by aqueous ammonia solutions in order to improve the preparation method and properties of the resulting film. The structural changes in the film were investigated by means of infrared spectroscopy.

## Experimental Section

The oligomer solution was prepared from methyltriethoxysilane (MTES). MTES and an aqueous nitric acid were mixed in a mole ratio of  $\text{MTES}:\text{H}_2\text{O}:\text{HNO}_3 = 1:1.25:2 \times 10^{-4}$  in which  $\text{HNO}_3$  was introduced as the hydrolysis catalyst. A magnetic stirrer was used for complete mixing. After reaction for 2 days, 2 moles of  $\text{C}_2\text{H}_5\text{OH}$  was evaporated for each mole of MTES by means of a vacuum evaporator at 40 °C. Then aluminum acetylacetonate ( $\text{Al}(\text{acac})_3$ ) and  $\text{H}_2\text{O}$  were added to the solution in the ratio of  $\text{Al}(\text{acac})_3:\text{H}_2\text{O}:\text{MTES} =$

0.001:0.5:1. It was expected that this chelate compound could depress the precipitation of crystalline octamethylsilsesquioxane ( $(\text{CH}_3\text{SiO}_{3/2})_8$ ).<sup>5</sup> The mixture was stirred at 50 °C until it became homogeneous. After being kept at 40 °C for 15 h, the oligomer solution thus obtained was poured onto immiscible aqueous solutions and gelled on them to form self-sustained gel films.

Table 1 shows various solutions used for the film experiments. Four samples were prepared on an aqueous solution containing 16 wt % of NaCl and 7 wt % of  $\text{C}_2\text{H}_5\text{OH}$  in which NaCl was introduced to increase the density and  $\text{C}_2\text{H}_5\text{OH}$  for the complete spreading of the oligomer solution.<sup>4</sup> For each sample, 3 mL of the oligomer solution was poured onto the 350 mL supporting solution in a plastic tray (30 cm  $\times$  20 cm), which was modified so that other liquids could be introduced to replace the solution without changing the liquid level. After 5 h, the supporting solution of three film samples was substituted by aqueous ammonia solutions whose pH's were 9, 10, and 12, respectively. After being kept for 48 h, these films were taken out, rinsed in distilled water for 30 min, and dried on plastic substrates in air. Aqueous nitric acid of pH 1 was also used to replace the supporting solution. For comparison, the oligomer solution was directly poured onto ammonia solutions, and the gelation behavior was observed as well.

The films were investigated by means of FTIR attenuated total reflectance (ATR). A Ge prism with an incidence angle of 45° was employed.

## Results

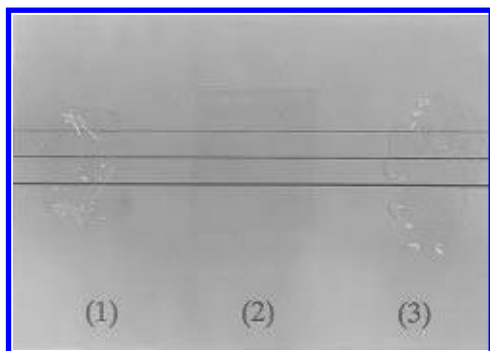
**(1) Formation of Gel Films.** A drop of oligomer solution completely spread on the supporting solution and gelled in less than 2 h. A difficulty was encountered in taking the film out. Initially, the gel film was very deformable and sticky as in the previous report.<sup>4</sup> The stickiness decreases with time, and the film could be scooped out of the supporting solution after 2 days' aging. When the supporting solution was substituted by ammonia solutions, the stickiness disappeared quickly. This change became more appreciable with an increase of pH. In addition, shrinkage of the gel film was observed when the supporting solution was substituted by high pH ammonia solutions. No shrinkage was observed when no substitution was made and the ammonia solution of pH 9 was used for substitution, whereas the shrinkage was 6% and 12% for the

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**TABLE 1: Solutions Used in the Film Experiments<sup>a</sup>**

samples	supporting solutions	substitution solutions
film 0	aqueous solution (NaCl, C <sub>2</sub> H <sub>5</sub> OH)	untreated
film 1	aqueous solution (NaCl, C <sub>2</sub> H <sub>5</sub> OH)	N1, pH = 9
film 2	aqueous solution (NaCl, C <sub>2</sub> H <sub>5</sub> OH)	N2, pH = 10
film 3	aqueous solution (NaCl, C <sub>2</sub> H <sub>5</sub> OH)	N3, pH = 12
film 4	aqueous solution (NaCl, C <sub>2</sub> H <sub>5</sub> OH)	H, pH = 1
	N2, pH = 10 N3, pH = 12	

<sup>a</sup> Aqueous solution contains 16 wt % of NaCl and 7 wt % of C<sub>2</sub>H<sub>5</sub>OH. N1, N2, and N3 represent aqueous ammonia solutions of pH 9, 10, and 12, respectively. H represents aqueous nitric acid of pH 1.

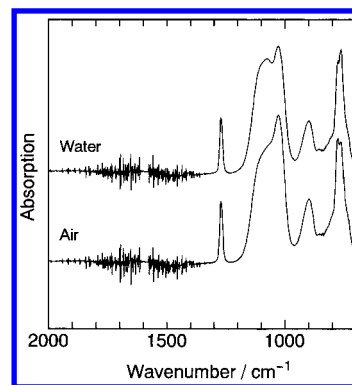


**Figure 1.** Photograph of gel films. (1) indicates the untreated sample (film 0). The film was prepared without the treatment by ammonia solution and scooped out after 48 h aging. The puckers were caused by the stickiness when it was transferred onto a plastic substrate. (2) indicates the sample treated by ammonia solution of pH 10 (film 2). The drying method was the same as that of untreated sample. (3) indicates the film prepared by pouring the oligomer solution onto ammonia solution of pH 10 (film 4).

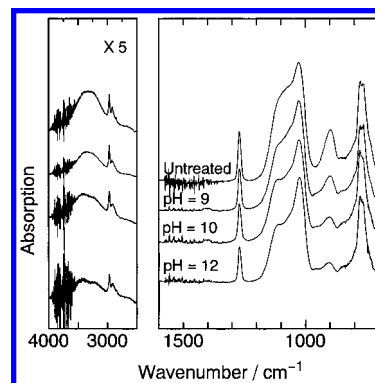
ammonia solutions of pH 10 and 12, respectively. The untreated sample (film 0) and the sample treated by an ammonia solution of pH 10 (film 2) are shown in Figure 1. When the untreated sample was transferred onto a plastic substrate, puckers were formed easily because of the deformability and the adhesion to the substrate. The flatness is greatly improved by the substitution of the supporting solution.

When the oligomer solution was poured directly onto the ammonia solutions of pH 10 and 12, it gelled immediately, and no uniform gel film was obtained. For comparison, the sample prepared on an ammonia solution of pH 10 (film 4) is also shown in Figure 1. Many fringes are seen in this sample, and there is a large variation in the thickness. On the other hand, when aqueous nitric acid of pH 1 was used to replace the supporting solution, no evidence for the enhancement of hardening was obtained.

**(2) Infrared Spectroscopy.** Infrared spectra of the four samples are shown in Figures 2 and 3. The assignments of the main absorption bands can be found in the literature.<sup>6</sup> The absorption at 1270 cm<sup>-1</sup> is assigned to the absorption of Si-CH<sub>3</sub>. The absorption from 1000 to 1220 cm<sup>-1</sup> is assigned to the asymmetric stretching vibration of Si-O-Si bonds, and the one at 900 cm<sup>-1</sup> is assigned to the stretching vibration of Si-OH. The broad band at 3300 cm<sup>-1</sup> arises from OH vibrations of silanols, hydrogen-bonding silanols, and adsorbed water.<sup>7</sup> The absorption at 2900 cm<sup>-1</sup> is attributed to the vibrations of methyl groups.<sup>6</sup> In the untreated sample (film 0) (Figure 2), some difference in the absorption band from 1000 to 1200 cm<sup>-1</sup> is



**Figure 2.** ATR spectra of CH<sub>3</sub>SiO<sub>3/2</sub> gel film (film 0). The film was not treated by ammonia solution. The curve designated "Water" is the spectrum of the side of the film that was in contact with the supporting solution during the formation of gel film. The curve with the word "Air" is the spectrum of the side that was in contact with air.



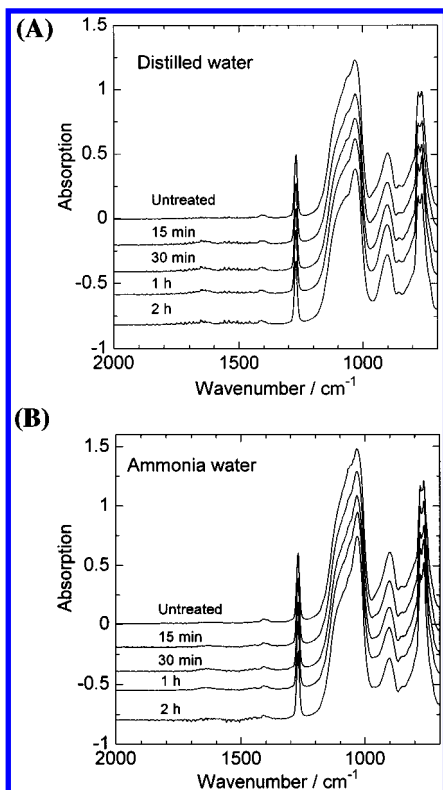
**Figure 3.** ATR spectra of CH<sub>3</sub>SiO<sub>3/2</sub> gel films (films 0–3). All of them were measured on the side of the film that was in contact with air.

seen between the two surfaces and the absorption at 1030 cm<sup>-1</sup> is relatively weak on the side of the aqueous solution. In the other three films treated on ammonia solutions, however, no appreciable difference was observed between their two surfaces.

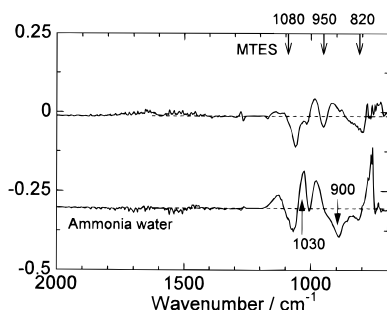
Figure 3 shows that with an increase of pH of the ammonia solution, the absorption at 1030 cm<sup>-1</sup> increases at the expense of the absorptions at 1100 and 900 cm<sup>-1</sup>. Correspondingly, the 3300 cm<sup>-1</sup> absorption decreases relative to the absorption of methyl groups at 2900 cm<sup>-1</sup>.

To clarify the structural change at the early stage, the oligomer solution was directly coated onto Ge prisms (the coating layer having a thickness of ~100 μm).<sup>8</sup> After drying in air for 2 h, they were inserted in distilled water and an ammonia solution of pH 10, respectively. The ATR spectra were recorded at various treatment times and are shown in Figure 4. For comparison, the subtraction spectra were calculated for the 2 h spectra and are shown in Figure 5. Ethanol shows a very strong peak around 1050 cm<sup>-1</sup>. The decrease of ethanol in the gel film may contribute to the decrease of the absorption in this region. The increase of pH increases the absorption at 1030 cm<sup>-1</sup> at the expense of the absorption at 900 cm<sup>-1</sup>, as seen in Figure 3. A decrease at 820 cm<sup>-1</sup> can be noticed in both of the subtraction spectra. When the oligomer solution was further kept for 100 h at room temperature and smeared on the prisms, such a change at 820 cm<sup>-1</sup> was found to be less remarkable after similar treatments. Since the precursor, MTES, shows strong absorption bands at 1080, 950, and 820 cm<sup>-1</sup>, the decrease at 820 cm<sup>-1</sup> may result from the hydrolysis of ethoxy groups remaining in the gel film.

The spectral results indicate that ammonia solutions promote



**Figure 4.** ATR spectra of coating film on Ge prism. The coating film was prepared by smearing the oligomer solution on Ge prism. Part A shows the spectra measured after treatments in distilled water for various times. The absorption scale refers to the spectrum of untreated sample. Part B shows the spectra measured after treatments in ammonia water of pH 10. The absorption scale refers to the spectrum of untreated sample.



**Figure 5.** Subtraction spectra of the 2 h samples. Each of them is obtained by subtracting the spectrum measured prior to the treatments from the spectrum measured after treatment for 2 h. The absorption scale refers to the sample treated in distilled water.

the polymerization of Si—OH bonds in the gel film,<sup>9</sup> which resembles a structural change caused by a heat treatment.<sup>10</sup>

## Discussions

When the gel film is in contact with an aqueous solution, H<sub>2</sub>O, NH<sub>3</sub>, and C<sub>2</sub>H<sub>5</sub>OH may be transferred across the interface. The progress of the hydrolysis reaction seen in Figures 4 and 5 can be attributed to the migration of water into the gel film. In addition, Figure 2 indicates that there is a little difference in the polymerization between the two surfaces. According to Brown et al.,<sup>11</sup> the asymmetric vibration of cyclotrisiloxanes appears at about 1030 cm<sup>-1</sup>. On the side of the aqueous solution, more water is available and similarly deformed bonds are expected to decrease because of a structural rearrangement, Si—OH + Si—OH ↔ Si—O—Si + H<sub>2</sub>O, as proposed for the rehydration of dried silica gel.<sup>12</sup> This mechanism seems to

account for the relative decrease at 1030 cm<sup>-1</sup> (Figure 2). With the introduction of NH<sub>3</sub>, the polymerization is greatly enhanced probably because of a base-catalyzed condensation mechanism as in solution.<sup>13</sup> With the propagation of polymerization, ethanol arising from the hydrolysis probably becomes difficult to be accommodated in the gel film. This leads to the shrinkage of the gel film on the ammonia solutions.

It is assumed that the stickiness depends on the concentration of Si—OH groups. The adhesion behavior of the oligomer solution was investigated on various substrates. When it was coated onto a PMMA substrate, the gel film strongly adhered to the substrate after drying. This, however, was not true with other films such as PE, PP, and PS films. A hydrogen bonding across the interface due to Si—OH bonds probably enhances the adhesion,<sup>14</sup> which occurs with the carbonyl group in PMMA. As seen in Figure 4, the concentration of Si—OH bonds remains essentially unchanged when the film was in contact with distilled water. Therefore, the gel film remains flexible and appears sticky when in contact with itself or with other substrates. However, on an ammonia solution, the gel film becomes rigid and the stickiness disappears due to the enhanced polymerization.

The spreading behavior of the oligomer solution on the aqueous solution changed with the interface energy.<sup>4</sup> When the reaction in the oligomer solution proceeded to high degrees, the spreading area tended to decrease. The interface energy was assumed to increase with a decrease of the number of Si—OH bonds in the oligomer solution. To prepare a uniform gel film, there should be enough time for an oligomer solution to spread over a supporting solution before the gelation, and a rapid change in the interface energy should be avoided at the gelation point. When the present oligomer solution is poured directly onto an ammonia solution with a high pH, both the interface energy and the viscosity are expected to change dramatically because of the enhanced polymerization. It is possible that the oligomer solution fails to spread uniformly over the ammonia solutions with pH's of 10 and 12.

The present results indicate that formation of a gel film on a neutral or acidic aqueous solution and subsequent introduction of ammonia solution for promoting the polymerization reaction after gelation provide an effective method for preparing a flat CH<sub>3</sub>SiO<sub>3/2</sub> film. This method shortens the time on the supporting solution and reduces the concentration of Si—OH in the gel film.

## Conclusions

The method of preparing thick gel films on the supporting solution can be greatly improved by increasing the pH of the supporting solution after the gelation. The stickiness disappears quickly, and the time necessary for preparing the gel film is very much shortened. Furthermore, gel films with lower Si—OH concentrations can be obtained without heat treatment. These improvements can be attributed to the acceleration of condensation of silicic gel components under basic conditions.

## References and Notes

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