Colloid Polym Sci 275:744–753 (1997)
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ORIGINAL CONTRIBUTION

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Diffuse reflectance infrared Fourier transform spectral study of the interaction of 3-aminopropyltriethoxysilane on silica gel. Behavior of amino groups on the surface

Received: 18 November 1996
Accepted: 14 February 1997

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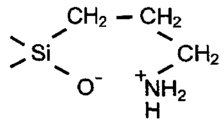
Abstract Three silica gel sample systems, modified with 3-aminopropyltriethoxysilane (APTS), were prepared by sequentially sampling the reaction mixture at various time intervals, and the diffuse reflectance infrared Fourier transform (DRIFT) spectra of these samples were measured in the regions 2700–3500 and 1300–2000 cm^{-1}. The IR bands observed at 1597 and 1629–1633 cm^{-1} were assigned to the deformation modes of NH_2 and NH_3^+ groups, respectively. The intensities of these two bands are dependent on both the APTS concentration used in the preparation and the reaction time. The results are summarized as follows. For the sample systems in which smaller APTS concentration were used, most of the NH_2 groups of the aminopropyl segments are converted into the NH_3^+ groups on the surface, showing that the $SiO^- \cdots H^+NH_2$-type structure is predominantly stabilized on the surface of the silica gel. As the APTS concentration in the reaction mixture increases, the population of NH_2 groups in the silane layer coated onto the surface increases. Interpretation of the CH stretch region further suggests that cyclic structures may be formed on the surface as a consequence of the formation of NH_3^+ groups.

Key words DRIFT – APTS – silica gel – NH_2 behavior

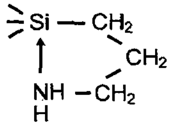
Introduction

The macroscopic nature [1–3] and molecular structure [4–12] of organosilane layers coated onto substrates has been extensively studied because of their great significance in industrial applications. One of the most commonly used silanes is 3-aminopropyltriethoxysilane (APTS), which differs from many other organotrialkyloxy silanes, in that it is very stable, even in aqueous solution. In order to explain this stability, Plueddemann [13] proposed structural models of five- or six-membered rings in which the nitrogen atom either interacts with the Si atom or one of the SiOH groups. Structural models of special relevance to this present study may be cited. Boerio et al. [14] studied an aminosilane layer coated onto the surface of electropolished metal, using infrared reflection absorption spectroscopy, and assigned the IR bands at 1510 cm^{-1} to the NH_3^+ characteristic mode as a consequence of the ring structure (I), and the band at 1575 cm^{-1} to the five membered ring structure (II).

(I)



(II)



Anderson et al. [15] examined an aminosilane layer coated onto a silicon wafer, using X-ray photoelectron spectroscopy for chemical analysis (ESCA). The results provided evidence for the existence of protonated amine. Moses et al. [16] also studied the ESCA spectra of aminosilane layers deposited onto the surface of an electrode. As a consequence, they proposed two six-membered ring models, which contain the $Si–O^- \cdots HN^+H(R)–$ and $SiOH \cdots NH(R)–$ structures.

Ishida et al. [6] proposed two structural models (which depended upon the degree of curing) in which the aminopropyl segment can be either a ring structure involving the $SiO^- \cdots H \cdots {}^+NH_2–$ structure or an extended structure of aminopropylsilyl segments. Furthermore, they [17] investigated FTIR and laser Raman spectra of 3-aminopropyltriethoxysilane and its analogs in aqueous solution and in the solid state, and concluded that the residual SiOH groups are strongly hydrogen bonded to the amino groups in the form of $SiOH \cdots NH_2$ rather than as $SiO^- \cdots {}^+NH_3$.

They also noted [17] that the molecular structure of an aminosilane layer deposited onto the surface of a substrate may depend on both the degree of curing and the concentration of silane used for the silane-substrate reaction.

Recently, we have found that a time-dependent conformational change of a 3-aminopropylsilyl segment occurs on the surface of silica gel [18], indicating that structural changes of amino silane layer may occur in the process of curing.

It is well known that amines (for example, triethylamine) form very strong hydrogen bonds with silanols on the surface of a substrate and that the bonded amine renders the Si–O group of the silanol more nucleophilic [19, 20]. Tripp and Hair [21] have reported on the process for base promoted silanization in a chlorosilane–silica gel system. Thus, behavior of the NH_2 groups on the surface of a substrate must play an important role in the process of silanization and therefore should be further investigated.

In the present study, a series of samples of silica gel modified with different concentration of APTS was prepared under equilibrium conditions and three other sets of samples were also prepared by sequentially sampling the reaction mixture of silica gel of increasing size and a constant concentration of APTS, at various time intervals. Diffuse reflectance FTIR and FT-Raman spectra of these samples were used to investigate the behavior of NH_2 groups on the surface of the silica gel, since these analytical techniques have proved to be very powerful in characterizing the chemical structure of a silane coating layer [7–9]. In particular, the concentration and time dependence of the spectra are discussed in detail with respect to the behavior of NH_2 groups on the surface.

Experimental

Super Micro Bead Silica Gel B-5 (SMBS), with a particle size distribution of $d_{10}/d_{90} = 1.5$, average particle diameter 5 μm, and pore diameter $\phi = 5.5$, 6.6 and 8.1 nm, was purchased from Fuji Silysia Chemical Co. Particle diameter and pore diameter were determined by the coulter counter method [22] and mercury porosimetry [23], respectively. Surface areas (A) were determined by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption (a surface area of 16.2 Å was assumed for molecular N_2): the A values were 498, 512 and 437 $m^2\,g^{-1}$ for $\phi = 5.5$, 6.6 and 8.1 nm, respectively. 3-Aminopropyltriethoxy silane (APTS), obtained from Shinetsu Chemical Industry Ltd., was used for the reaction with SMBS without purification.

The four SMBS sample systems (A ($\phi = 5.5$ nm), B ($\phi = 6.6$ nm), C ($\phi = 6.6$ nm) and D ($\phi = 8.1$ nm) were modified with APTS. The A samples were prepared as follows. SMBS (40 g) in toluene (120 ml) was refluxed with stirring at 423 K. APTS was added to the preheated SMBS–toluene mixture, and refluxed for 6 h with stirring (under these conditions the reaction was completed). The concentration of APTS in the reaction mixture was varied over six concentrations within the range 0.08–0.72 $mol\,l^{-1}$ (Table 1). The SMBS–APTS–toluene mixture was separated from the reactor, and the reaction was quenched by washing with methanol. The unreacted ethoxy groups in the substrate were hydrolyzed in the water–methanol (1:1) solution for 2 h at room temperature [24]. The APTS modified SMBS was again washed with methanol and dried at 388 K under vacuum. Thus, six samples modified with different APTS concentrations were prepared (samples A; A-1 to A-6). An A sample of SMBS treated under the same conditions but in the absence of APTS was also prepared (control SMBS). These A samples can be regarded as the aminopropylsilyl (APS)–SMBS complexes prepared under equilibrium conditions.

For preparation of the B, C and D sample systems, the substrate was sequentially sampled at various time intervals. The concentrations of APTS in the toluene solution were 0.051 $mol\,l^{-1}$ for B, 0.17 $mol\,l^{-1}$ for C and 0.57 $mol\,l^{-1}$ for D. The temperature of the reaction mixture in the reaction vessel was kept at 388 K for the three sample systems. Each substrate sample extracted at various time intervals was treated as described for the A samples and was then dried at 388 K under vacuum. B (B-1 to B-7) and C (C-1 to C-7) were extracted at time intervals of 60, 180, 300, 600, 900, 1800 and 7200 s, respectively. For D samples (D-1 to D-7) the time intervals were 60, 300, 600, 900, 1800, 3600 and 21 600 s. These samples (A, B, C and D) were assumed to be in a fully dehydrated state, since the samples were not heated above 388 K [25].

Table 1 Concentrations of bound-APS (C^C (APS, μmol m^{-2}) and C^N (APS, μmol m^{-2})) determined from carbon and nitrogen content

Sample	t (s)	C^C	C^N	Yield (%)	C (APTS, mol l^{-1}) in toluene
A-1		1.21	0.36	72	0.08
A-2		1.39	0.74	74	0.19
A-3		2.82	1.81	91	0.28
A-4		3.60	3.36	67	0.72
B-1	60	0.35	0.24		0.05
B-3	600	0.38	0.25		
B-5	1800	0.39	0.25		
B-7	7200	0.45	0.25	83	
C-1	60	1.25	1.02		0.17
C-2	300	1.38	1.05		
C-3	600	1.43	1.05		
C-4	900	1.47	1.05		
C-5	1800	1.52	1.05		
C-6	3600	1.59	1.05		
C-7	7200	1.64	1.05	105	
D-1	60	2.11	1.59		0.57
D-2	180	2.32	1.81		
D-3	300	2.46	1.93		
D-4	600	2.59	2.06		
D-5	900	2.65	2.10		
D-6	1800	2.83	2.25		
D-7	21600	3.31	2.55	85	

For the four sample systems thus obtained, it was confirmed that the DRIFT spectra coming from the APTS–ethoxy groups and the ^{29}Si NMR line coming from the APTS- ^{29}Si atom completely disappeared.

A Yanaco-CN Coder MT 600 was used for elemental analysis (carbon and nitrogen) of the samples. The concentration of APTS reacted with the silica gel was determined by analyzing the nitrogen content of the *A* and *D* samples. Since the dependence of nitrogen content on reaction time for the *B* and *C* samples was very small, although the carbon content increased as the reaction proceeded, the concentration of bound APS (C(APS)) for these samples was determined from the carbon atom content, and the data are listed in Table 1.

The diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a Nicolet Magna System 750 at 4 cm^{-1} resolution using the Spectra Tech Collector diffuse reflectance accessory at room temperature. Samples mixed with dried KBr were used to fill the DRIFT sample cup before measurement. The reproducibility of the DRIFT band frequencies was ± 2 cm^{-1}.

Raman spectra were recorded with a Nicolet 950 Fourier transform Raman spectrometer (4000–150 cm^{-1}) using Nd:YAG laser (CVI) excitation wavelength of 1064 nm with a resolution of 4 cm^{-1} at room temperature. The reproducibility of the band frequencies was accurate to ± 1 cm^{-1} for sharp bands and ± 2–3 cm^{-1} for broad and weak bands. The Raman spectra were obtained from pressed solid samples in a capillary tube with a laser power of 440 mW.

The ^{29}Si NMR spectra were recorded on a Varian UNITY-400 spectrometer operating at 79.5 MHz at 25 °C. The ^{29}Si chemical shifts (ppm) are given relative to an external 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) standard. The ^{29}Si NMR spectra were measured using an acquisition time of 0.102 s, contact time of 2.5 ms, recycle time of 15 s, and pulse width of 6.3 μs. The high resolution solid state ^{29}Si NMR measurements were achieved by applying a cross polarization sequence (XPOLAR). The spectra with CP were measured by cross polarization and magic angle spinning (CP MAS). The spectra without CP were measured using only MAS (designated NCP). The two types of spectra were integrated and then the CP correction factors were obtained from division of the NCP integral values by the CP integral values for each resonance line. Thus, the real integral values were calculated from multiplication of the CP integral values with the CP correction factors.

A Rigaku TG 8101D was used for thermogravimetric analysis. The contents of water absorbed on the control SMBS and APS-bound SMBS samples were checked by thermogravimetric analysis: ca. 1.5% for control SMBS and ca. 1.0% for APS-bound samples.

Results and discussion

Figure 1 shows the correlation between the APS-concentration (C^C(APS)) determined from the carbon content and that (C^N(APS)) determined from the nitrogen content. For the *D* samples, there is an excellent proportional linear relationship. For the *A* samples, also the linear relationship holds, but there is considerable scatter in the data. However, we may conclude that the C^C and C^N values reflect qualitatively the amounts of APS segments bound onto the surface of silica gel at various concentrations for the *A* and *D* samples, although it is difficult to evaluate the absolute values. Accordingly, the C^C and C^N values of these sample systems can be used to discuss qualitatively the variation of bound APS concentration.

Conversely, for the *B*- and *C*-samples, there is no proportional relationship between the C^C and C^N values, since the analytical percentages for nitrogen are very close to the identification limit. However, both the C^C and C^N values of these two sample systems lie on (or very close to) the proportional linear relationship for the *A*- and *D*-sample systems. Moreover, the C^C values for the *B*- and *C*-sample systems increase exponentially with an increase in reaction time, although the C^N values give the appearance

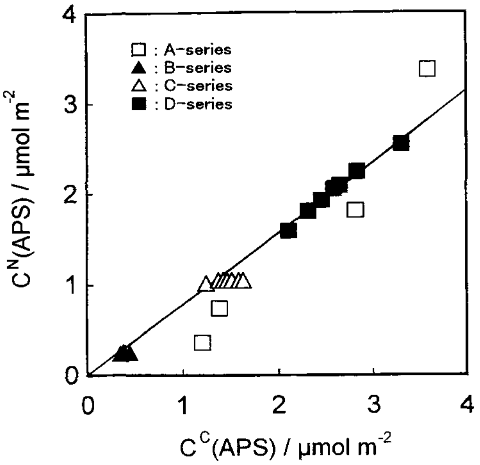


Fig. 1 Plots of C^N(APS) against C^C(APS) for the four sample systems (□: sample *A*; ▲: sample *B*; △: sample *C*; ■: sample *D*)

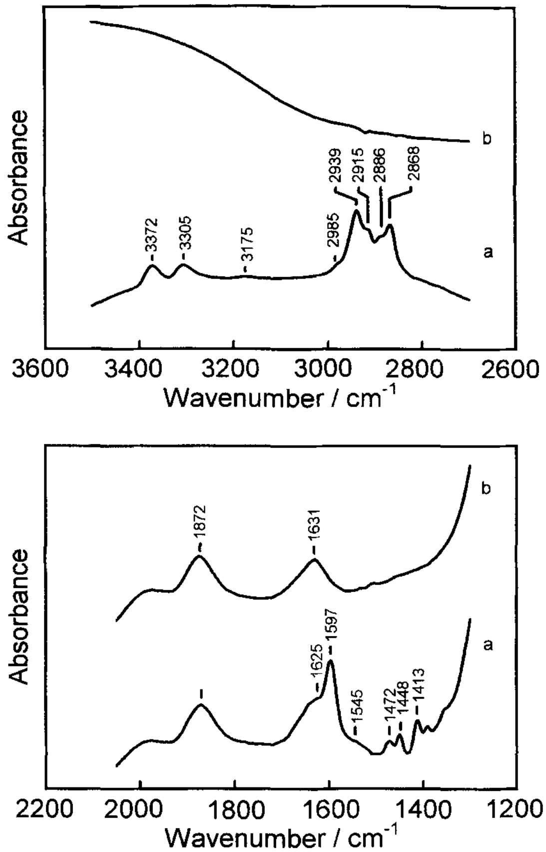


Fig. 2 DRIFT spectrum of an APS-SMBS complex (sample *A*-4, concentration of bound APS = 3.36 μmol m^{-2}): a, prepared under equilibrium conditions; b, control SMBS

of being time invariant. Thus, the C^C values for these systems can also be used to discuss qualitatively the variation of bound-APS concentration.

In this present paper, the dependence of the DRIFT spectra on both the APTS-concentration used in the preparation of these four sample systems and on the reaction time is qualitatively discussed.

Figure 2 shows a representative DRIFT spectrum (sample *A*-4) of the APS–SMBS complexes in the regions 1200–2000 and 2700–3500 cm^{-1} and also the spectrum of control SMBS. The observed band frequencies and a tentative assignment [6] are listed in Table 2.

In this spectrum, the asymmetric and symmetric NH_2 stretch modes ($\nu_{asy}(NH_2)$ and $\nu_{sym}(NH_2)$) are observed at 3305 and 3372 cm^{-1}, respectively (data not shown). When the APTS molecules are in the monomer state in toluene, the ν_{asy} and ν_{sym} modes are observed at 3324 and 3384 cm^{-1}, respectively. Therefore, the two $\nu(NH_2)$ bands of bound APS shift downward about 12–19 cm^{-1}, indicating that the NH_2 groups of bound APS moieties are concerned in formation of hydrogen bonding networks. Very weak and broad IR bands at 3150–3200 cm^{-1} arising from the NH_2 stretch modes reveal that some of the NH_2 groups participate in a strong hydrogen bonding system.

The IR band at 1597 cm^{-1} may be assigned to the NH_2 deformation mode ($\delta(NH_2)$) of bound APS moieties. Since the $\delta(NH_2)$ mode arising from the free NH_2 group of APTS is observed at 1605 cm^{-1}, the $\delta(NH_2)$ band of bound APS is shifted downwards approximately 8 cm^{-1}. This shift possibly depends on the strength of the hydrogen bond, and may imply that most of the NH_2 groups of bound APS moieties participate in formation of a weak hydrogen bonding system.

Table 2 Observed band frequencies (cm^{-1}) for the DRIFT spectrum of *A* sample (*A*-4) and tentative assignments[a]

Frequency[b]		Assignment[c]
3372	w	$\nu_{as}(NH_2)$
3305	w	$\nu_s(NH_2)$
2939	s	$\nu(CH_2)$
2915	sh	
2886	sh	
2868	s	
1625	sh	$\delta_{asm}(NH_3^+)$
1597	s	$\delta(NH_2)$
1472	w	$\delta(CH_2)$
1448	w	
1413	w	$\delta(Si\text{–}\underline{CH_2})$

[a] Ref. [6].
[b] s, strong; w, weak; sh, shoulder.
[c] ν, stretch; δ, bend.

A similar observation has been made by Morimoto et al. [26] for the IR spectrum of *n*-butylamine. Liquid *n*-butylamine exhibits an IR band at 1605 cm^{-1} which can be assigned to the NH_2 deformation mode, and the band shifts to 1580 cm^{-1} in $CHCl_3$.

Silverstein and Bassler [27] reported that the NH_3^+ groups furnish symmetrical and asymmetrical deformation vibration bands in the regions 1550–1504 and 1600–1575 cm^{-1}, respectively. The IR bands at 1515 and 1610 cm^{-1} for *n*-butylamine hydrochloride, which have been reported by Morimoto et al. [26], correspond well to the asymmetric and symmetric NH_3^+ deformation modes in the two regions.

In this present study, we have measured the IR spectrum of γ-aminobutyric acid hydrochloride in order to confirm the presence of NH_3^+ bands. The IR bands observed at 1512 and 1628 cm^{-1} were assigned to symmetrical and asymmetrical NH_3^+ deformation modes, respectively.

The very weak IR bands at 1414, 1448 and 1472 cm^{-1} are assigned to the CH_2 deformation mode of *n*-propyl chain for bound APS moieties [28].

$\delta(NH_2)$ band behavior of APTS–SMBS complexes

Figure 3 shows the DRIFT spectra in the 1400–2000 cm^{-1} region for the series of *A* samples (*A*-1 to *A*-4) which were prepared under equilibrium conditions. In particular, it should be noted that the features of the bands at 1597 and 1630 cm^{-1} depend on the concentration of bound APS moieties. That is, as the concentration of bound APS increases, the 1597 cm^{-1} band increases while that of the 1630 cm^{-1} band decreases.

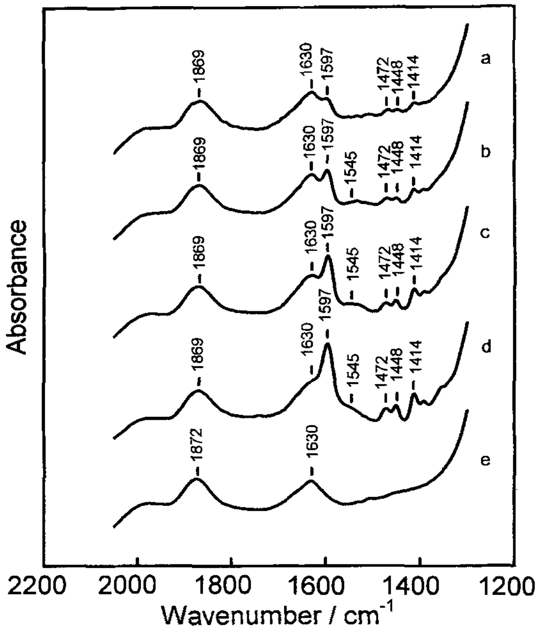


Fig. 3 DRIFT spectra of the *A* sample system (a, *A*-1; b, *A*-2; c, *A*-3; d, *A*-4) and control SMBS (e) in the 1200–2000 cm^{-1} region

In the DRIFT spectra of the APS–SMBS complexes, there exists the possibility for superimposition of the IR band at 1630 cm^{-1} (arising from H_2O bending modes of water adsorbed on silica gel) upon the asymmetric NH_3^+ deformation band, since the 1630 cm^{-1} band is also observed in the spectrum of control SMBS (Fig. 3e). The difference spectra, obtained by subtracting the IR spectrum of control SMBS from that of the APS–SMBS complex, indicate the presence of a 1630 cm^{-1} IR band arising from the vibrational modes of APS moieties in the absence of adsorbed water and this band can be assigned to the asymmetric NH_3^+ deformation. The conclusion remains that behavior of the NH_2 groups varies as the concentration of bound APS increases.

In order to understand more clearly the behavior of the NH_2 groups of the silane-layer coated onto the surface of SMBS particles, the DRIFT spectra of three sample systems (*B*, *C*, and *D*), which were prepared by sequentially sampling at the various time intervals, were also investigated in detail.

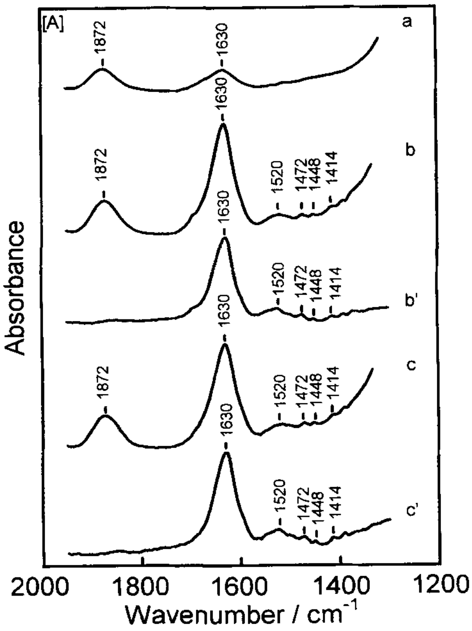
Figure 4 shows the DRIFT spectra and the difference spectra (corrected for control SMBS) for the *B*, *C* and *D* sample systems in the 1400–2000 cm^{-1} region.

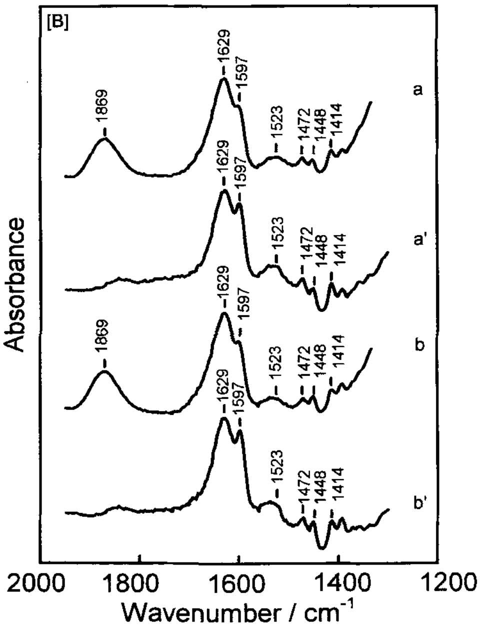
For *B* samples (Fig. 4A) prepared by sampling at 60 and 7200 s, a strong and broad 1630 cm^{-1} band arising from the asymmetric NH_3^+ deformation modes is predominant, in addition to a very weak and broad 1520 cm^{-1} band which may be assigned to the symmetric NH_3^+ deformation band. Furthermore, the 1597 cm^{-1} band arising from the $\delta(NH_2)$ modes of NH_2 groups does not appear for this sample system. This observation indicates that most of the NH_2 groups of bound APS moieties were converted into NH_3^+ groups during preparation of the *B* samples.

Vrancken et al. [11, 12] have discussed how water molecules adsorbed on the surface of silica gel induce hydrolysis of APTS-ethoxy groups, leading to SiOH groups which can combine to form a siloxane linkage. This process induces production of a new water molecule as surface water. The presence of this surface water may play an important role in the conversion of the $NH_2 \rightarrow NH_3^+$, which, in turn, will be reflected in the DRIFT spectra of these sample systems.

In the DRIFT spectra of the *C* sample system (Fig. 4B), the 1597 cm^{-1} band is clearly seen beside the predominant 1629 cm^{-1} band, indicating that while the NH_2 groups are mostly converted into NH_3^+, either a small part remains unconverted or a $NH_3^+ \rightarrow NH_2$ conversion partially occurs. Dependence of relative absorbance R^{1597} ($=A^{1597}/A^{1867}$) and R^{1633} ($=A^{1633}/A^{1867}$) on reaction time appears to be very small, since the former values are almost constant for all *C* samples (Fig. 5, curve a). Weak and broad bands at 1520–1523 cm^{-1} may be assigned to symmetric NH_3^+ deformation modes.

On the other hand, for the *D* sample system, in which a higher APTS concentration (0.57 mol l^{-1}) was used for the APTS–SMBS reaction, the spectral features in the region near 1600 cm^{-1} depend markedly upon reaction time (Fig. 4C). As the reaction proceeds, the intensity of the 1597 cm^{-1} band increases while that of the 1633 cm^{-1} decreases, showing that the population of the NH_2 groups increases while that of NH_3^+ decreases. It is evident that the intensity of the 1597 cm^{-1} band reflects the rate of variation of the NH_2 environment, since the relative absorbance A^{1597}/A^{1876} increases exponentially with reaction time, as seen in Fig. 5, curve b. Decrease in intensity of the 1633 cm^{-1} band with increasing reaction





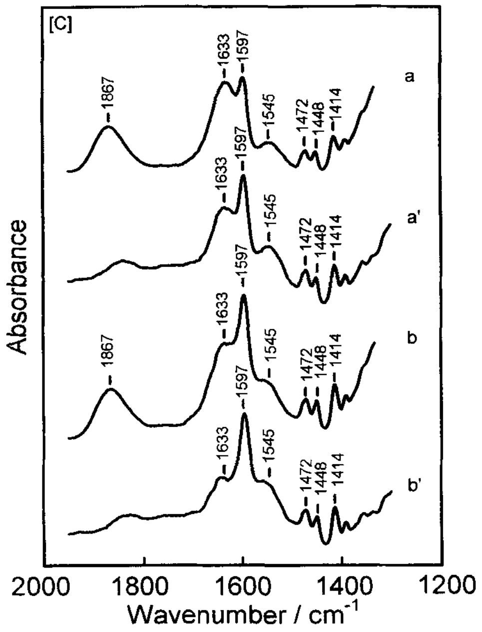


Fig. 4 DRIFT spectra of the *B* ([A]), *C* ([B]) and *D* ([C]) sample systems and the difference spectra in the 1200–2000 cm^{-1} region ([A]: a, control SMBS; b, *B*-1; b′, the difference spectrum for *B*-1; c, *B*-7; c′, the difference spectrum for *B*-7. [B]: a, *C*-1; a′, the difference spectrum for *C*-1; b, *C*-7; b′, the difference spectrum for *C*-7. [C]: a, *D*-1; a′, the difference spectrum for *D*-1; b, *D*-7; b′, the difference spectrum for *D*-7)

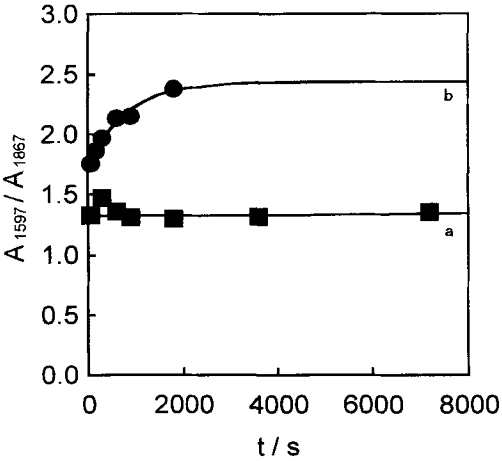


Fig. 5 Dependence of relative absorbance A_{1597}/A_{1867} on reaction time for a, *C* and b, *D* samples

time probably suggests that the NH_3^+ groups are converted into NH_2 groups. For the four sample systems, we have confirmed by using the difference spectrum method that further adsorption of water molecules brings about a decrease in intensity of the 1629–1633 cm^{-1} band arising from the NH_3^+ groups and an increase in intensity of the 1597 cm^{-1} band. Accordingly, we may assume that the $NH_3^+ \rightarrow NH_2$ conversion is promoted by adsorbed water molecules. Therefore, the time dependence of the 1597 cm^{-1} band intensity also contains a contribution from the rate of the $NH_3^+ \rightarrow NH_2$ conversion, in addition to that from the rate of appearance of NH_2 which is a consequence of the APTS–SMBS reaction. For the *D* samples, kinetic analysis of the data for relative absorbances A^{1597}/A^{1876} was also carried out by assuming a pseudo-first-order reaction for the rate of variation of the 1597 cm^{-1} band intensity to yield a rate constant equal to $k = 1.72 \times 10^{-3}\ s^{-1}$.

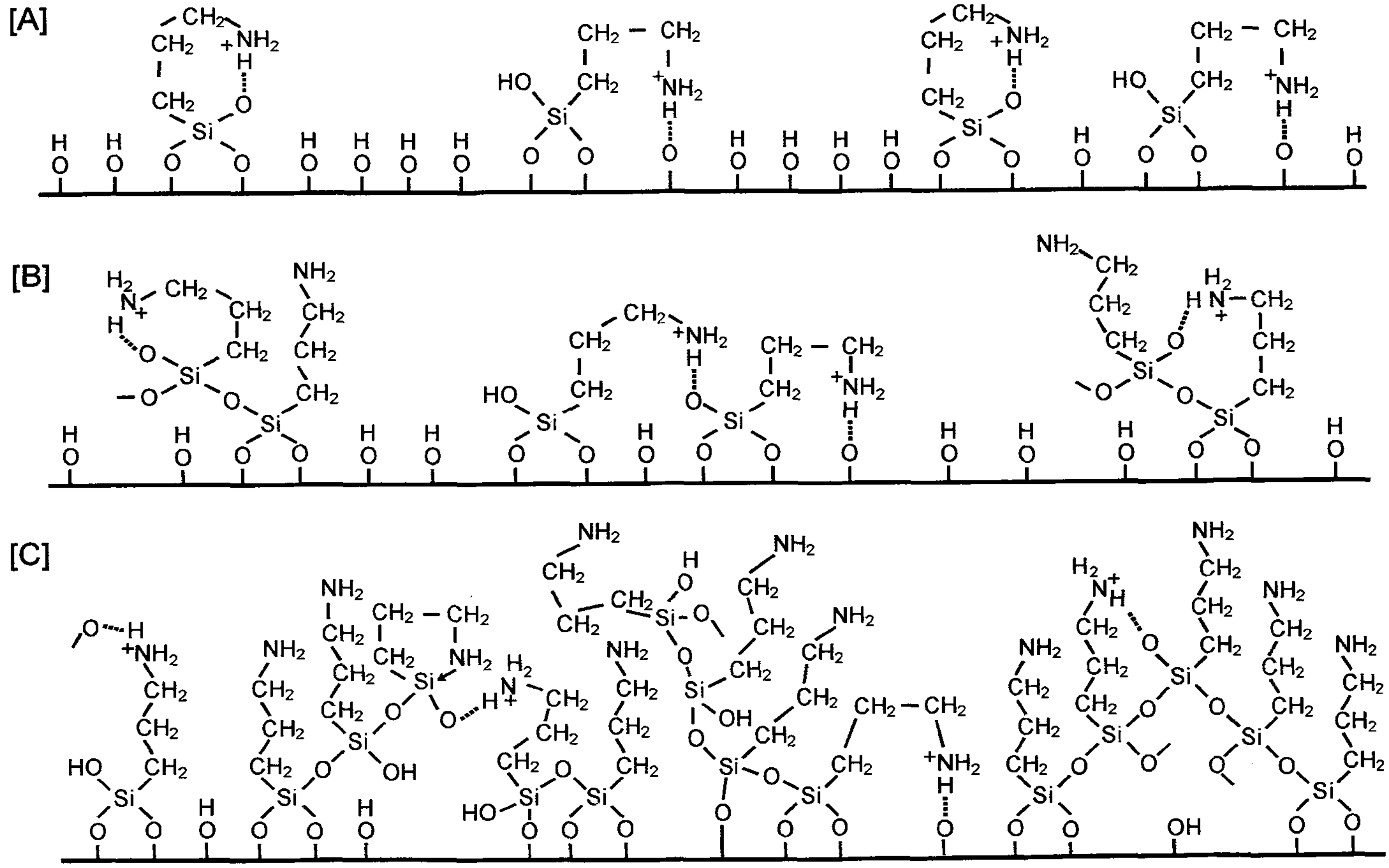
For the *D* samples, the very broad bands at 1540–1570 cm^{-1} tend to increase slightly in intensity as the reaction proceeds. We may assign these bands to the $\delta(NH_2)$ modes of NH_2 groups coordinated to the Si atom in a cyclic structure, thereby endorsing the formation of a cyclic intramolecular type complexes (the so-called Pluedemman type complex) on the surface of the substrate when the sample in this system was treated with a higher APTS concentration.

Chiang et al. [17] assigned the IR band observed at 1561 cm^{-1} for APTS modified silica gel to the deformation mode of NH_2 groups with strong hydrogen bonding.

Schrader and Block [29] proposed a model for a nonring dimeric structure, in which one end of each dimer in the APS layer is chemically adsorbed onto the glass surface. Chiang et al. [6] examined a silica gel sample treated with 1% w/w APTS aqueous solution and proposed a model for hydrogen bonding within the $SiO^- \cdots H{-}NH_2^+$ group. Their results showed that most of the amino-silane molecules were adsorbed on the surface of the silica gel and that the amino groups were oriented and chemically adsorbed onto the surface.

Thus, the behavior of NH_2 groups of bound APS segments strongly depends on the concentration of APTS in toluene used for the modification, as shown schematically in Fig. 6. We may therefore assume that NH_3^+ groups

Fig. 6 A possible schematic structure for APS-SMBS complexes ([A], *B* samples; [B], *C* samples; [C], *D* samples)



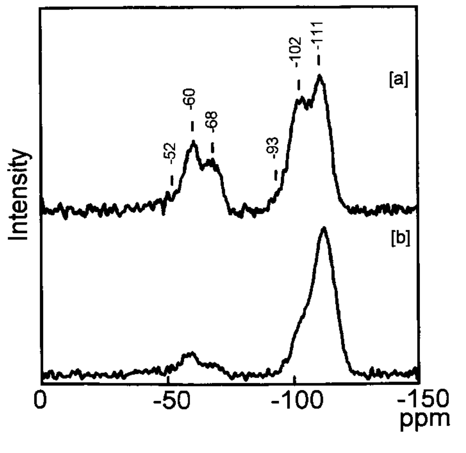
are predominant on the surface of the substrate for a sample system treated with a very little dilute APTS solution (*B* and *C* samples) while the population of NH_3^+ on the surface decreases as the concentration of APTS used for the modification increases (*D* samples). Moreover, for the *D* sample system a five membered ring structure may be present within the siloxane polymers or oligomers.

Characterization of the SMBS surface by ^{29}Si NMR and NH_3^+ formation

For one of the *D* samples, *D*-7 (C(APS) = 2.55 μmol m^{-2}, see Table 1), the ^{29}Si CP/MAS NMR spectrum was measured (Fig. 7a). The observed resonance signals at −52, −60 and −68 ppm were ascribed to the ^{29}Si nuclei of the (–O)Si(OH)$_2$C–, (–O)$_2$Si(OH)C– and (–O)$_3$SiC– groups of APS moieties bound on the SMBS particles, respectively [30–32]. The signals at −93, −102, and −111 ppm were assigned to the ^{29}Si nuclei of the (–O)$_2$Si(OH)$_2$, (–O)$_3$SiOH and (–O)$_4$Si groups belonging only to the SMBS particles, respectively [30–32].

For the same sample, the ^{29}Si MAS spectrum was also measured without applying a cross-polarization sequence (Fig. 7b). The ^{29}Si signal intensities were corrected by the CP correction factors determined from the integral intensities of both the CP/MAS and MAS spectra (the correction factors were 0.47, 0.92, 0.96 and 1.96 for the ^{29}Si resonance lines at −60, −68, −102 and −111 ppm, respectively). The total corrected integral intensities of the three ^{29}Si signals belonging only to the SMBS particles should be independent of the concentration of bound APS, while those of the three signals arising from only bound APS will depend on the concentration of APS moieties bound on the SMBS particles. When the total corrected integral intensities of the three signals arising only from the SMBS particles are placed equal to 100, the total corrected integral intensities I_t(APS) of the three ^{29}Si signals arising from bound APS moieties may be expressed by relative corrected integral intensities (I_r(APS) [%] = [100 I(APS)]/[I((–O)$_3$SiOH) + I((–O)$_4$Si)].

Fig. 7 ^{29}Si CP/MAS ([a]) and MAS ([b]) spectra of the *D*-7 sample (reaction time: 21 600 s)



In our previous paper [33], we showed that the total relative corrected integral intensities are proportional to the concentration of bound APS moieties and that the APS-concentration per unit area may be calculated both from the relative corrected integral intensities and the modified APTS quantities. In a similar fashion, we may calculate the concentrations of the (–O)$_3$SiOH and (–O)$_4$Si species arising from the SMBS particles by use of reduction coefficients (C μmol m^{-2}/relative corrected integral intensity for each signal of bound APS).

The values of I(APS), I((–O)$_3$SiOH) and I ((–O)$_4$Si), which were obtained from the ^{29}Si NMR spectra of the *D*-7 sample, are 14.22%, 20.40% and 79.60%, respectively. Therefore, we can estimate quantitatively the concentrations of the (–O)$_3$SiOH and (–O)$_4$Si species belonging only to the SMBS particles of the *D*-7 sample. The C((–O)$_3$SiOH) and C((–O)$_4$Si) values are 3.66 and 14.27 μmol m^{-2}, respectively. When we assume that one molecule of APTS reacts with one (–O)$_3$SiOH group on the surface, the total concentration of (–O)$_3$SiOH species for SMBS particles untreated with APTS molecules (C^t((–O)$_3$SiOH)) may be placed equal to the total of C(APS) and C((–O)$_3$SiOH) (C^t((–O)$_3$SiOH) = C(APS) + C((–O)$_3$SiOH)). The percentage of (–O)$_3$SiOH species reacted with APTS molecules (P_r) may be given by P_r [%] = 100 C(APS)/C^t((–O)$_3$SiOH). If it is assumed that the C(APS) value is equal to that (2.55 μmol m^{-2}) calculated from the carbon content, then the P_r is equal to 35%, implying that 65% of the total concentration of (–O)$_3$SiOH species (C^t = (2.55 + 3.66 =) 6.21 μmol m^{-2}) remains uncondensed. This estimation means that one bound-APS moiety is surrounded by the two (–O)$_3$SiOH groups on the surface of the SMBS particles.

For the *B* and *C* samples, measurement of the ^{29}Si NMR spectra of bound APS moieties was not successful, because of the very small concentrations of bound APS moieties. However, if we assume that the C^t((–O)$_3$SiOH) value (6.21 μmol m^{-2}) for the *D*-7 sample may be applied to the *B* and *C* samples, then the P_r values for these samples can be easily calculated to yield values for the *B* and *C* samples equal to 21% and 7%, respectively. Therefore, for the *B* and *C* samples, most of (–O)$_3$SiOH species remain unreacted and one bound-APS moiety is surrounded by four or more (–O)$_3$SiOH groups.

Thus, we may assume that an increased population of $(-O)_3SiOH$ species brings about an increase in interaction of the $APS-NH_2$ groups with silanols, since the number of reactive hydroxyl groups increases as the number of $(-O)_3SiOH$ species surrounding each $APS-NH_2$ group increases [34, 35].

When a small concentration of APTS is used for the modification, then the size of the silane oligomers must become small. Therefore, we may speculate that the extent of interaction of silane oligomers with $(-O)_3SiOH$ groups increases as the size of the oligomers decreases, resulting in formation of the $Si-O^- \cdots H-NH_2^+$ structure.

For the *B* samples, it may be assumed that most of the NH_2 groups of bound APS moieties form NH_3^+, since the size of any bound APS oligomers will be small.

When the oligomers increase in size, we may expect steric hindrance to prevent interaction of the $APS-NH_2$ groups with the hydroxyl groups of the silica gel. Therefore, growth of oligomers may bring about an increase in the number of unconverted NH_2 groups as evidenced by the $\delta(NH_2)$ band at 1597 cm^{-1}. Such is the case for the *C* samples (Fig. 4B).

When a higher APTS concentration is used for the sample preparation, the size of the silane oligomers probably becomes larger and the number of unconverted NH_2 groups increases as the reaction proceeds, bringing about a still further increase in the number of NH_2 groups. Thus, the $\delta(NH_2)$ band increases in intensity, as seen in the DRIFT spectra of the *D* samples (Fig. 4C).

Evidence for a cyclic structure in the CH stretch region

When the APS moieties bound on silica gel form $SiO^- \cdots H-NH_2^+$ groups, we may expect the propyl segments of APS moieties to take up sterically bent structures involving gauche forms, as shown in Fig. 6. It is well known that the $\nu(CH)$ modes of a hydrocarbon chain containing gauche forms appear at a higher frequency, compared with those of extended hydrocarbon chains [36, 37]. In particular, for compounds containing cyclic hydrocarbons, the $\nu(CH)$ modes of the methylene groups are observed at a higher frequency near 3000 cm^{-1} [38]. If the formation of NH_3^+ occurs as a consequence of an internal hydrogen bounded six-membered ring, then the cyclic structure should be reflected in the $\nu(CH)$ band frequency.

Figures 8A and C show the DRIFT and Raman spectra, respectively, of the *A* sample system in the $\nu(CH)$ mode region. As the concentration of APTS used for the reaction decreases, IR bands at 2857, 2957 and 2992 cm^{-1} and the corresponding Raman bands at 2859, 2958–2960 and 2996 cm^{-1} become more intense. The IR bands at 2957 and 2992 cm^{-1} and the corresponding Raman bands may be assigned to the $\nu(CH)$ modes characteristic of a cyclic hydrocarbon structure, since corresponding IR and Raman bands are also found for cyclic compounds like butyrolactone and 2-pyrolidinone [39]. The $\nu(CH)$ bands characteristic of a cyclic structure are also observed at 2960 and 2996–3000 cm^{-1} in the DRIFT spectra of the *B* samples (Fig. 8B), for which a smaller APTS concentration was used in the preparation. The appearance of the 2960 and 2997 cm^{-1} bands may be regarded as evidence for the $\nu(CH)$ mode in such a cyclic structure.

If Plueddemann's cyclic structure is formed on the surface of silica gel, the $\delta(NH_2)$ modes of the NH_2 groups should be observed at 1570–1580 cm^{-1}, since the $\delta(NH_2)$ bands for an NH_2 group of this type should be located near the 1597 cm^{-1} band of the NH_2 type. However, in the DRIFT spectra of the *B*, *C* and *A* (*A*-1 and *A*-2) samples,

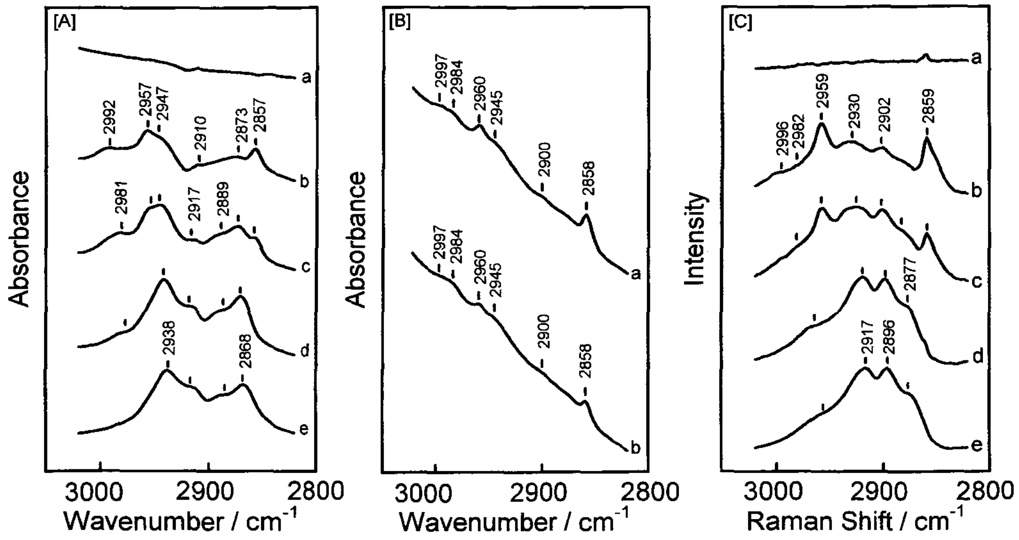


Fig. 8 DRIFT spectra of the *A* ([A]) and *B* ([B]) sample systems in the CH stretch region ([A]: a, control SMBS; b, *A*-1; c, *A*-2; d, *A*-3; e, *A*-4. [B]: a, *B*-5; b, *B*-7) and FT-Raman spectra of the *A* sample system ([C]: a, control SMBS; b, *A*-1; c, *A*-2; d, *A*-3; e, *A*-4)

no bands were observed which corresponded to the 1570–1580 cm^{-1} band. We therefore conclude that a Plueddemann-type structure is absent for these samples.

When we compare the spectrum for the *A*-4 sample (Fig. 3, spectrum d) with that for the *D*-7 sample (Fig. 4C, spectrum b), the 1545 cm^{-1} band for the *A*-4 sample is observed as a shoulder while that for the *D*-7 sample appears as a peak with greater intensity than that for the *A*-4 sample. This observation may be explained as follows. For the *A*-4 sample, the 1570–1580 cm^{-1} band appears and increases in intensity, reducing the appearance of the 1545 cm^{-1} band to a shoulder. For the *D*-7 sample we must assume that the intensity of the 1570–1580 cm^{-1} band is smaller than that for the *A*-4 sample, since the spectrum show a distinct trough in this region. Therefore, the possibility of the presence of a Plueddemann-type structure exists for the *A*-4 and *D*-7 samples. From the difference in the intensities of the 1570–1580 cm^{-1} band between the two samples, it may be assumed that the population of this type of structure for the *A*-4 sample is larger than that for the *D*-7 sample. This difference may be due to the difference in the conditions used for preparation of the two samples (in particular, the difference in temperature: 423 K for the *A*-series and 388 K for the *B*-, *C*- and *D*-series).

In the DRIFT and Raman spectra of the *A* samples, as well as the *B* samples, it should be noted that as the APTS concentration decreases the intensity of the bands at 2857 cm^{-1} (IR) and 2859 cm^{-1} (Raman) increases, while that of the bands at 2873 cm^{-1} (IR) and at 2877 cm^{-1} (Raman) decreases. We have recently confirmed for an APTS-related compound that the ν(CH) modes arising from a CH_2 group adjacent to a Si atom appear in the 2860–2870 region [40]. Therefore, the 2857 and 2873 cm^{-1} bands may arise from the methylene group of a CH_2Si segment and the dependence of the intensity of these bands on APTS concentration probably reflects the variation in the environment of the CH_2Si segment which is occasioned by the APTS–SMBS reaction.

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