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SHORT COMMUNICATION

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13C- and 1H-NMR and FTIR spectroscopic evidence for aggregate formation of organosilanes in toluene

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Abstract Changes in the ^{13}C and ^{1}H NMR chemical shifts of the silane coupling agent (3-aminopropyltriethoxysilane, APTS) in toluene, which were detected as the concentration of APTS increased, have been interpreted in terms of the formation of micelles and the presence of a critical micelle concentration (CMC) equal to ca. 0.47 mol l^{-1}. For the protons of the *n*-propyl segment, ^{1}H NMR splitting patterns have been analyzed and conformations of the propyl segment have been discussed. Plots of relative absorbance of the two NH_2 stretch IR bands at 3324 and 3384 cm^{-1} against concentration provided an inflection point (corresponding to the CMC) at a value equal to 0.46 mol l^{-1}. Thus, consideration of the interaction of APTS with a surface must take into account the presence of both APTS aggregates as well as APTS monomers.

Key words 3-Aminopropyltriethoxysilane – CMC – reversed micelles

Introduction

Organosilane coupling agents are commonly used to reinforce the mechanical properties of the interface between two different materials through the chemical functions of silane molecules. However, the mechanism of this reinforcement has not yet been completely elucidated.

Nishio et al. [1] have used Fourier transform near infrared attenuated total reflectance spectroscopy to study the process of dehydration of silanes on the surface of glass. Infrared spectra of silica gel, which had been allowed to react with γ-anilinopropyltrimethoxysilane (AnPS), have also been measured with a diffuse reflectance infrared spectrometer, and the molecular structure of the AnPS-coating layer formed on the surface of the gel has been discussed [2]. The results showed that the reactivity of silane molecules and the characteristics of reinforcement materials may be associated with the molecular structure of the silane-modified surface and that the conditions for silane treatment, including the pH, silane concentration of the silane solution, solvent and method of application all affect the mechanical properties of the material.

Recently, Nishio et al. [3] also investigated the effect of silane treatment on the interfacial transmissibility of glass fiber and showed that, although the interfacial transmissibility varies with silane concentration, there exists an optimum concentration for enhancement of interfacial strength, thus highlighting the important role of the concentration of silane modified on the material.

In this communication, we describe measurements of the ^{13}C-, ^{1}H-NMR and IR spectra of a silane–toluene system, taken under various concentrations of silane. These data lead to further understanding of the effect of silane on the mechanical properties of reinforced material. The dependence on concentration of the ^{13}C- and

^{1}H-NMR chemical shifts and NH stretch vibrational modes is discussed within the context of formation of reversed micelles of silane molecules in toluene.

Experimental

Materials

3-Aminopropyltriethoxy silane (APTS) was purchased from Shinetsu Chemical Industry Ltd., and was used without further purification. Toluene (Wako Chemical Industry Co., Ltd.) was distilled over metallic-Na and stored over $LiAlH_4$ before use in order to ensure that it was rendered anhydrous.

^{13}C-, ^{1}H-NMR and FTIR measurements

^{13}C NMR spectra were recorded on a JEOL JNM-GSX500 spectrometer operating at 125.65 MHz at 25 °C using an acquisition time of 1.088 s under deuterium internal lock and proton noise decoupling mode. Carbon-13 chemical shifts (δ, ppm) were determined by use of 65 536 points in the time domain. Tetramethylsilane (TMS) was used as an external reference and no susceptibility correction was made. All ^{13}C NMR measurements were made in 5 mm NMR sample tubes at 25 °C. The Fourier transform infrared (FTIR) absorption spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer at 4 cm^{-1} resolution, using a CaF_2 cell. The thickness of the sample solutions was 0.1 and 0.5 mm.

^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer operating at 199.975 MHz at 25 °C using an acquisition time of 10.992 s. Proton chemical shifts (^{1}Hδ, ppm), which are given relative to toluene–CH_3 signal as an internal reference, were determined by use of 65 536 points in the time domain. All ^{1}H NMR measurements were made in 5 mm NMR sample tubes at 25 °C.

In order to analyze the spin-coupling system, calculation of the ^{1}H NMR spectrum which gave a best fit with the observed spectrum was carried out with the program LAOCOONIII.

Results and discussion

Concentration dependence of ^{13}C NMR chemical shifts

The ^{13}C NMR spectra of APTS in toluene were measured at various concentrations. A representative ^{13}C NMR spectrum is shown in Fig. 1, together with assignment of the peaks and numbering of the carbon atoms.

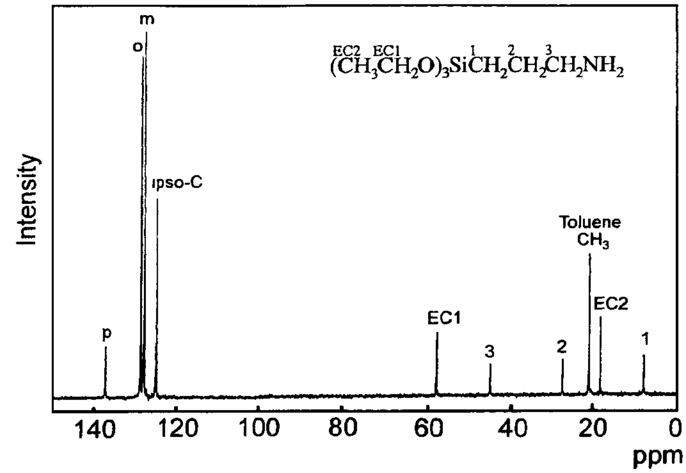

Fig. 1 ^{13}C NMR spectrum of APTS in toluene (0.7 mol l^{-1}) and the numbering of the carbon atoms

For the ethoxy carbons (EC1 and EC2), the ^{13}C chemical shifts moved upfield in a linear fashion with an increase in concentration, and this trend was ascribed to the weak solvation effect of toluene [4, 5]. We now emphasize the concentration dependence of ^{13}C chemical shift values for the *n*-propyl segment. Plots of the ^{13}C chemical shifts of the C-1, C-2 and C-3 carbon nuclei against the reciprocal of concentration are illustrated in Fig. 2. The concentration dependence of the ^{13}C chemical shifts for the C-1 carbon atom is very small. However, the ^{13}C resonance signals of the C-2 and C-3 nuclei shift markedly downfield as the concentration increases. In particular, it should be noted that the inflection point in the δ vs. C^{-1} plots for C-1, C-2 and C-3 nuclei occurs at approximately the same APTS concentration (0.46–0.47 mol l^{-1}).

This observation is very similar to that found for the variation of ^{13}C chemical shift which arises from formation of normal micelles in H_2O or of reversed micelles in non-polar solvents [6–9]. By analogy, we may ascribe the variation in ^{13}C chemical shift (δ) vs. C^{-1} plots (Fig. 2) to formation of aggregates and the concentration at the breakpoint to the critical micelle concentration (CMC) in toluene.

The downfield shift of the C-2 and C-3 carbon nuclei upon micellization is probably caused by the usual induction effect [10]. That is, APTS molecules aggregate to form reversed micelles in toluene, allowing hydrogen bonds to be formed between the NH_2 groups. Formation of a reversed micelle brings about a decrease in charge density for the C-2 and C-3 nuclei, thereby causing a downfield shift of the ^{13}C chemical shifts.

The small variation of the ^{13}C chemical shift for C-1 may be accounted for as follows. We may assume that the

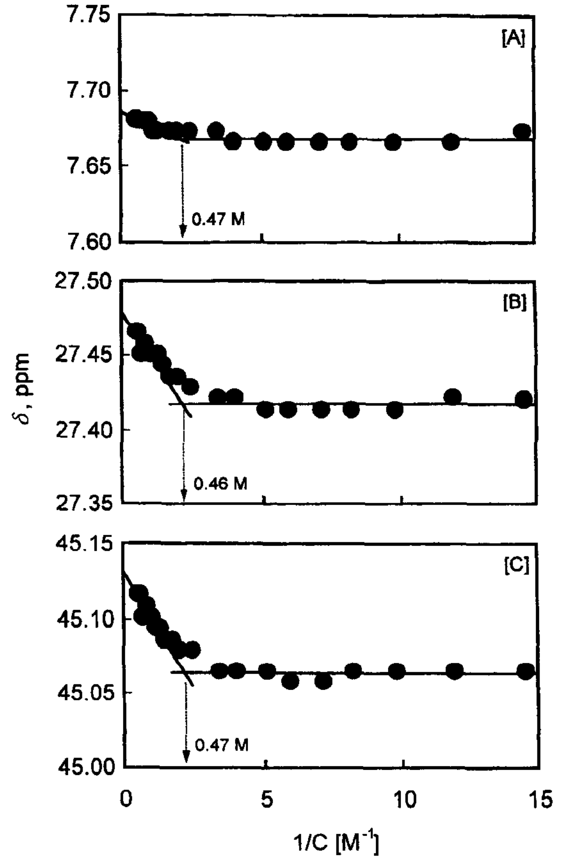

Fig. 2 Plots of ^{13}C NMR chemical shifts of C-1 [A], C-2 [B] and C-3 [C] carbon atoms against inverse concentration of APTS in toluene

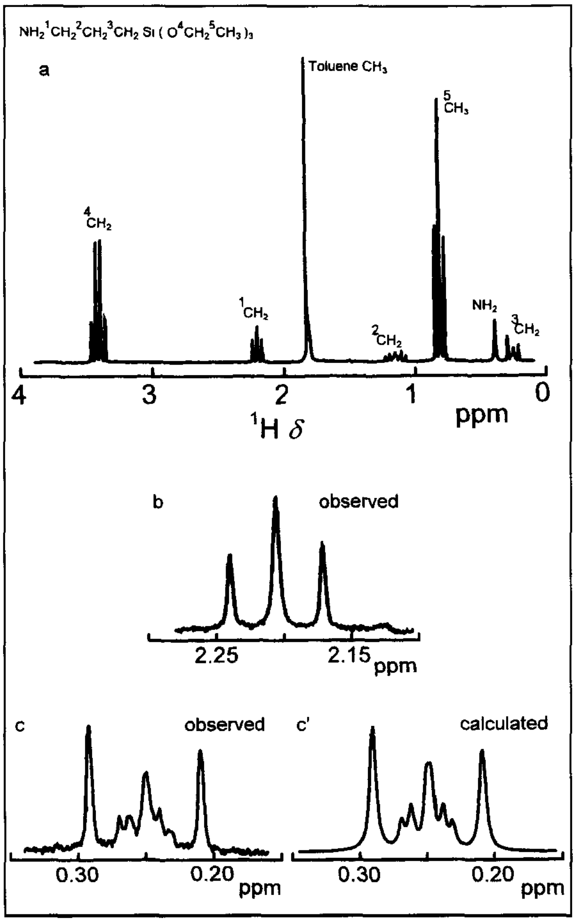

Fig. 3 Observed ^1H NMR spectrum (a) of APTS in toluene (1.4 mol l^{-1}) ((b) magnified spectrum of the $^1CH_2$ protons, (c) magnified spectrum of the $^3CH_2$ protons, (c') calculated spectrum of the $^3CH_2$ protons)

NH_2 groups, which are weakly bonded through a hydrogen bonding network, form the polar core in toluene, while the *n*-propyl segment and the three ethoxy groups are extended into the bulk phase. In this model, the C-1 carbon which is attached to the Si atom is likely to be more subject to solvation than are the C-2 and C-3 nuclei [5]. Since the C-1 nucleus is also subject to the induction effect [10], which may compete against the solvation effect, the result is likely to be a weak concentration dependence of the ^{13}C chemical shift of the C-1 carbon, as observed.

^1H NMR spectra and conformations about ^1C–^2C and ^2C–^3C bonds

The ^1H NMR spectrum of the APTS–toluene system and its assignment are shown in Fig. 3. The two protons of the NH_2 group provide a single peak, consequent upon a fast intermolecular exchange. In order to estimate the extent of formation of hydrogen bonds between the NH_2 groups, the ^1H NMR chemical shift ($^1H\delta$) of the NH_2 resonance peak has been measured at various concentrations (Fig. 4). It is evident that the inflection point in the $^1H\delta$ vs. C^{-1} plot occurs at a concentration equal to 0.48 mol l^{-1}, a value very close to the concentration (0.46–0.47 mol l^{-1}) of APTS at the breakpoint in the plots of $^{13}C\delta$ vs. C^{-1} (Fig. 2), thus providing confirmation of the value of the CMC. The downfield shift of the NH_2 resonance signal, which is observed as the concentration of APTS is increased beyond the CMC, is evidence of intermolecular hydrogen bond formation.

The protons of the $^1CH_2$ and $^3CH_2$ groups furnish splitting patterns which are typical of A_2X_2 and AA'XX' systems, respectively, and reflect the conformations about the ^1C–^2C and ^2C–^3C bonds, respectively. These spin-coupling systems have been analyzed by using the method

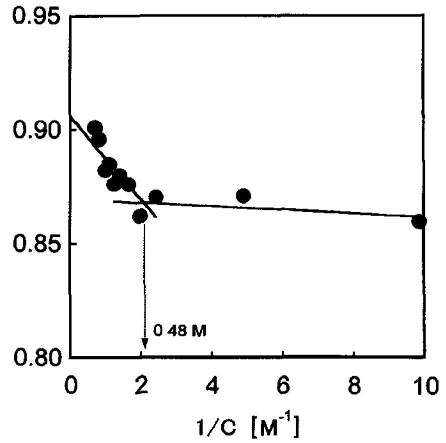

Fig. 4 Plot of the ^1H NMR chemical shifts of the NH_2 protons against inverse concentration of APTS in toluene

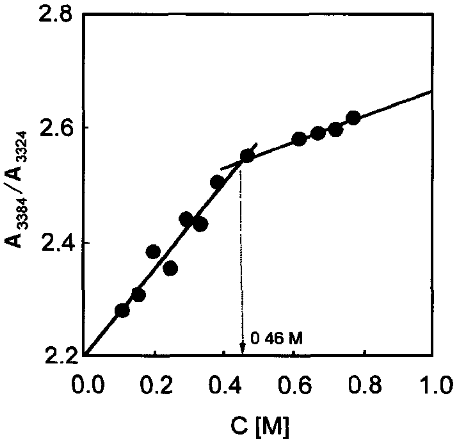

Fig. 5 Dependence of relative absorbance A_{3384}/A_{3324} on concentration of APTS in toluene

of Karplus [11], in order to examine the conformational change about the two skeletal C–C bonds. For the $^1CH_2$ spin-coupling system (Fig. 3b), the value of the coupling constant (J_{AX}) was 6.8 ± 0.2 Hz, indicating that the three rotational isomers (*trans* (T), *gauche* (G) and *gauche'* (G′) forms about the ^1C–^2C bond) are almost equally populated (fractional populations of the three isomers: $P_T = P_G = P_{G'} = 1/3$). This result implies that free rotation about the ^1C–^2C bond occurs in toluene.

For the $^3CH_2$ spin-coupling system (Figs. 3c and c′), an AA′XX′ system provided the best fit of the $^3CH_2$ spectral pattern, and the following coupling constants were obtained: $J_{AX} = 11.2$ Hz, $J_{AX'} = 5.2$ Hz, $J_{AA'} = -9.7$ Hz and $J_{XX'} = -8.3$ Hz. Unfortunately, we were unable to determine the fractional populations of the rotational isomers about the ^2C–^3C bond, since the coupling constants, J(T) and J(G), of the C–CH_2–CH_2–Si segment are not known. However, judging from the values of the coupling constants (J_{AX} and $J_{AX'}$) which were obtained from the best fit spectrum, we may assume that the *trans* form is probably predominant.

We examined the spectral patterns of these two spin-coupling systems at various concentrations. However, it was found that the values of the coupling constants are almost independent of APTS-concentration. This result reveals that micellization of the APTS–toluene system does not induce a conformational change of the propyl segment.

We may therefore speculate a model for the reversed micelle in the APTS–toluene system, in which the NH_2 groups, which participate in the formation of hydrogen bonds, constitute the polar core while the propyl triethoxy silane chains extend into the organic solvent.

Concentration dependence of NH_2 stretch IR band intensity

The IR spectra of the APTS–toluene solutions were also measured at various concentrations. The spectral features of the NH_2 stretch modes, asymmetric ($\nu_{NH_2}^{asy}$) and symmetric ($\nu_{NH_2}^{sym}$) stretch modes, were found to be dependent on concentration, and in dilute solutions their bands were observed at 3384 and 3324 cm^{-1}, respectively. These bands are very close in frequency to the 3392 and 3325 cm^{-1} bands which have been observed for typical straight chain amines [12]. Figure 5 shows the concentration dependence of absorbance of the 3384 cm^{-1} band (A_{3384}) relative to that of the 3324 cm^{-1} band (A_{3324}) and the value of A_{3384}/A_{3324} is seen to increase with increasing concentration. However, an obvious inflection point occurs at 0.46 mol l^{-1}, once again in good agreement with the CMC values (0.46–0.47 and 0.48 mol l^{-1}), derived from data in Figs. 2 and 4, respectively.

At higher APTS concentrations, it was found that within the NH stretch region of the IR spectrum a shoulder band at ca. 3300 cm^{-1} appears beside the 3324 cm^{-1} band and that its intensity increases with increasing concentration until the spectral feature approaches that of APTS in the liquid state. Therefore, this shoulder band may be regarded as the $\nu_{NH_2}^{sym}$ band arising from hydrogen bond formation between the NH_2 groups in the micelles. For APTS molecules in the liquid state, most of the silane molecules probably form aggregates held together by a network of hydrogen bonds, resulting in an apparent increase in the value of A_{3384}/A_{3324} consequent upon the decreased intensity of the 3324 cm^{-1} band.

We may assume from the differences in variation of the spectral features of the $\nu_{NH_2}^{asy}$ and $\nu_{NH_2}^{sym}$ modes that the symmetric stretch mode, but not that for the asymmetric stretch mode, depends strongly upon concentration. This result may indicate that a lone-pair on the NH_2 nitrogen atom is related to the hydrogen bonding system formed in an APTS aggregate, since the NH_2 symmetric stretch mode is sensitive to the state of hybridization of the N-atom, or to changes in hybridization [12].

Thus, the concentration dependence of the NH_2 stretch IR bands provides ample evidence for formation of hydrogen bonds between APTS molecules.

Concentration effect on the silane–substrate interaction

The results obtained from the ^{13}C NMR chemical shifts and the NH_2 stretch IR band indicate that above the CMC there exists a monomer $\rightleftharpoons$ micelle equilibrium in the silane solution. Accordingly, a discussion of the mechanism of interaction of silane on the surface of a material should take into account the effect of the presence of silane aggregates.

We have recently studied the kinetics of interaction of APTS on silica gel, using three different analytical techniques (DRIFT, ^{29}Si CP/MAS NMR and elemental analysis) [13, 14]. The results showed that a very fast initial reaction between APTS and silica gel is followed by competition between a slower second and a much slower third reaction. Moreover, it was suggested that there might be a chain reaction in the initial reaction process, leading to polymerization or oligomerization. Thus, when the surface of a material is treated with silane solution, we may assume that the concentration of silane modified on the surface subsequently affects the modified structure of the silane-coated layer, since the presence of silane aggregates may affect the degree of polymerization of silanes.

In our previous studies [15], we have shown that a local conformational change of aminopropylsilyl chains of siloxane polymers occurs on the surface of silica gel in the very fast initial reaction process and that this phenomenon depends strongly on the concentration of silane modified on the surface. Thus, we may assume that the formation of silane aggregates is closely associated with the modified structure of a silane-coated substrate.

Furthermore, for samples in which smaller APTS concentrations were used [16], we have shown that most of the NH_2 groups of the silane–aminopropyl segment are converted into NH_3^+ groups on the surface of silica gel, providing ample evidence that the structure of the silane-coated layer depends on the concentration of silane. Thus, study of the effect of silane aggregates on such a modification structure is highly desirable.

Conclusion

The ^{13}C- and ^{1}H-NMR chemical shifts of APTS in toluene were measured at various concentrations. The changes observed in the ^{13}C chemical shifts of the *n*-propyl carbon atoms and in the ^{1}H chemical shift of the NH_2 protons in solutions of increasing concentration of APTS, led to evaluation of a critical micelle concentration equal to 0.46–0.48 $mol\,l^{-1}$.

Analysis was made of the ^{1}H NMR splitting patterns for the protons of the $^{1}CH_2$ and $^{3}CH_2$ groups. The result showed that free rotation about the ^{1}C–^{2}C bond may occur and that a *trans* conformation about the ^{2}C–^{3}C bond is probably predominant.

Plots of the relative absorbance A_{3384}/A_{3324} of the NH_2 stretch IR bands at 3384 and 3324 cm^{-1} against concentration yielded a CMC value equal to 0.46 $mol\,l^{-1}$, in good agreement with those obtained from the plots of δ vs. $1/C$.

These observations led to the conclusion that APTS molecules form reversed micelles in toluene. Thus, any investigation of the interaction of silane on the surface of a substrate should take into account not only the silane monomer–substrate interaction but also the interaction between silane aggregates and substrate.

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