



# Comparison of model monomeric and polymeric alkyl stationary phases on silica using sum-frequency spectroscopy

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Received 18 June 2002; received in revised form 25 October 2002; accepted 5 November 2002

## Abstract

Model monomeric and polymeric stationary phases were examined using sum-frequency spectroscopy and contact angle measurements in order to determine structural differences between the two stationary phases. Octadecyldimethylchlorosiloxane (ODMS) monolayers and ODMS/methyl siloxane (MS) mixed monolayers in contact with water and acetonitrile solvent were examined. The results showed that the alkyl chains in the ODMS and the ODMS/TMS monolayer are highly disordered and are weakly sensitive to the change in solvent environment. In order to determine whether the observed disorder in ODMS is due to steric effects of the silicon bonded methyl groups or the lack of crosslinking, “surface-bonded” ODS and “highly crosslinked” ODS were studied and compared with ODMS. Calculations using contact angle data on ODMS monolayers showed that water interacts 70% with methyl groups and 30% with methylene groups.

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*Keywords:* Stationary phases, LC; Sum-frequency spectroscopy; Contact angles; Alkyl chain structure

## 1. Introduction

As the most widely used form of liquid chromatography, reversed-phase liquid chromatography (RPLC) has been used in the separation of an enormous number of compounds such as organic molecules, proteins, nucleic acids, and oligosaccharides. The basic strategy of this technique is to use a non-polar stationary phase, typically alkyl bonded silica, and a polar mobile phase. The analytes are then retained through a nonspecific hydrophobic interaction with the stationary phase. However, the

detailed mechanism of reversed-phase liquid chromatographic retention is complex and far from well understood due to the contribution of many factors, such as the composition, density, and conformation of the bonded phase, as well as the pretreatment of the silica substrate [1].

Alkylchlorosilanes are one of the most commonly used bonded reagents in RPLC. Among them, trifunctional chlorosilanes have been studied most extensively. It is well known that alkyltrichlorosilanes ( $\text{RSiCl}_3$ ) are very reactive and their reactions with silica depend strongly on the temperature, solvent, and surface or solution water [2–5]. In the presence of trace amounts of water, the  $-\text{Si}-\text{Cl}$  groups in alkyltrichlorosilanes are easily hydrolyzed, and then tend to undergo cross-linking, linear poly-

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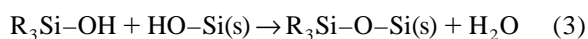
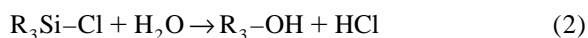
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merization, and to some extent covalent bonding to form siloxanes on the silica surface [6–8]. For long-chain alkyltrichlorosilanes (e.g. octadecyltrichlorosilane, ODS), in an all-trans conformation, highly stable self-assembled monolayers can be obtained due to the lateral cross-linking and strong van der Waals chain–chain interactions. Studies have shown that like alkyltrichlorosilanes, the use of alkyldichlorosilanes ( $R_2SiCl_2$ ) as the bonding reagents often resulted in cross-linking and linear polymerization [9,10]. Columns prepared with these materials have high alkyl chain density, but the mass-transfer and the chromatographic efficiency for most compounds are poor.

On the other hand, monofunctional alkylchlorosilanes have only one hydrolyzable group in the molecules, so they cannot cross-link or copolymerize with each other once they bond to the silica substrate. As a result, reactions of silica with monofunctional alkylchlorosilane (e.g. octadecyldimethylchlorosilane, ODMS) are generally preferred in the preparation of the stationary phase in RPLC because of their simple chemistry and higher reproducibility. Numerous studies in this area concerning the reaction conditions, dynamics, and bonded layer structure on porous and highly dispersed silica have been conducted [11–13]. It is generally accepted that as with alkyltrichlorosilanes and alkyldichlorosilanes, surface hydroxyl groups are required in order to graft monofunctional alkylchlorosilanes onto the silica surface, and the reaction differs in the vapor and solution phase [14]. In the vapor phase, the alkylchlorosilane reacts directly with the surface hydroxyl group, as is shown below:



where R represents the alkyl chains in the monofunctional alkylchlorosilane and the three alkyl chains can be of different lengths,  $HO-Si(s)$  represents a silanol on the silicon oxide surface. The reaction in the solution phase is more complex and includes the hydrolyzation of the alkylchlorosilane, as shown below:



For fundamental studies of stationary phase interfaces, alkylchlorosilanes are often grafted onto single surfaces, such as glass, silicon wafers, and quartz. However, little fundamental work on monofunctional alkylchlorosilane grafted surfaces has been done and great inconsistencies in the formed monolayer properties such as the water contact angle and its dependence on chain length still exist. For example, the advancing water contact angle ranges from  $50^\circ$  to  $117^\circ$  [15–19]. McCarthy et al. [19] pointed out that unlike alkyltrichlorosilane, the reaction of monofunctional alkylchlorosilane with silica is a very slow process, especially in the later stage of the reaction, and a long time (several days) are often required to achieve a complete monolayer. Therefore, the inconsistencies in water contact angle are mainly due to insufficient reaction time and many of the studies may involve incomplete monolayers. Furthermore, the alkyl chain conformation of the formed monolayers is still far from well understood. Duchet et al. [17] grafted alkyldimethylchlorosilane ( $CH_3(CH_2)_nSi(CH_3)_2Cl$ ,  $n$  varies from 4 to 30) onto silica glass plates and evaluated the orientation of the chains by combining ellipsometry, AFM, and FT-IR. They found that the alkyl chains were disordered for short alkyl chain ( $n < 18$ ) and became well organized with long alkyl chains ( $n \geq 18$ ), which was attributed to the strong chain–chain interactions. By studying the water contact angle of a series alkyldimethylsiloxyl surfaces ( $n$  ranges from 1 to 22), Fadeev and McCarthy [19] found that the contact angles were independent of the chain length, suggesting that the surfaces were quite disordered with the methyl groups pointed toward the water phase.

The retention process in RPLC also depends on the nature of the elution solvent and the distribution of the solute between the mobile and stationary phase. This process involves the transfer of the solute from the bulk mobile phase into or onto the stationary phase, and is especially complex for binary solvent systems in which microheterogeneities may form. Stalcup et al. [20] and Alvarez-Zepeda et al. [21] found that at high acetonitrile concentrations in acetonitrile and water mixtures the enthalpic contribution to the overall retention of polycyclic aromatic hydrocarbons was independent of the composition, while the contribution of the

entropy increased with the increasing water content. Carr and Harris [22] found that the alkyl chains in a C<sub>18</sub> chromatographic stationary phase collapsed in water, but with the addition of acetonitrile, the alkyl chain became more ordered because the acetonitrile penetrated into the monolayer, causing an increase in volume, polarity, and thus improving the alkyl chain order. However, for close-packed highly crosslinked ODS monolayers on fused-silica, no solvent-induced conformation change was observed [23,24].

Currently, the most commonly used bonded-phase silica is modified with ODMS, but tailing is still a problem during the separation process. The reason lies in the high density of unreacted silanols, which create negatively charged sites on the surface and thus slows the desorption kinetics by the strong electrostatic interaction. One of the ways to solve the tailing problem is to use mixed self-assembled monolayers, such as prepared from the mixture of octadecyltrichlorosilane and chlordinethylsilane. In this way, the excess silanol groups are converted to methyl groups. Furthermore, the alkyl chain density is also reduced, which increases the partitioning of the mobile phase and improves the separation.

In order to better understand the retention mechanism of RPLC and therefore better control the separation process, more detailed in situ studies of the conformation of the stationary phase of chromatographic interfaces and the effects of solvents are necessary. Sum-frequency (SF) spectroscopy is a powerful tool in the study of molecular conformation at many interfaces [25]. The theory of SF spectroscopy has been described in detail elsewhere [26,27]. Generally speaking, SF is a second-order nonlinear optical process, which is forbidden within media with inversion symmetry in the electric dipole approximation and is therefore a highly surface specific technique. In order to obtain SF signal, two laser beams are required, one tunable in the IR region ( $\omega_{\text{IR}}$ ), and the other one in the visible region ( $\omega_{\text{vis}}$ ). When the two laser beams overlap at the sample surface, a second-order signal at the SF ( $\omega_s = \omega_{\text{IR}} + \omega_{\text{vis}}$ ) is generated. When any of the three frequencies approaches a surface resonance, the SF signal is resonantly enhanced and yields a SF spectrum of the interface.

In this paper, the conformation of ODMS and ODS monolayers on a fused-silica substrate was

studied by in situ SF spectroscopy. Using SF spectroscopy, we have previously studied the solvent effects on mixed self-assembled monolayers of ODS and methyl siloxane (MS) on fused-silica substrates [24]. These studies showed that in these mixed monolayers, significant disorder could be induced in the alkyl chains by the solvent environment, especially in water. For comparison, the effect of solvents on the structure and conformation of ODMS and TMS (chlorotrimethylsilane, (CH<sub>3</sub>)<sub>3</sub>SiCl) mixed monolayers is examined here. In addition, the solvent-induced conformational change of the ODS-MS mixed monolayers were compared. In order to determine whether the observed disorder in ODMS is due to steric effects of the silicon bonded methyl groups or the lack of crosslinking, “surface-bonded” ODS [19] and “highly crosslinked” ODS were studied and compared with ODMS.

## 2. Experimental section

### 2.1. Materials

Octadecyldimethylchlorosilane (95%), chlorotrimethylsilane (TMS), ethyldiisopropylamine (95%), deuterated water (D<sub>2</sub>O), and deuterated acetonitrile (CD<sub>3</sub>CN) were purchased from Aldrich and used without further purification. Sulfuric acid and hydrogen peroxide were analytical grade and obtained from EM Science. Anhydrous toluene, acetone, and methanol were HPLC grade and obtained from Fisher Scientific. Deionized (DI) water was obtained with a Barnstead NANOpure system. Fused silica slides (50×25×1 mm) were purchased from Chem-Glass, Inc.

### 2.2. Substrate pretreatment

Fused silica slides were rinsed with acetone followed by DI water and dried under high purity nitrogen. The slides were then immersed in “piranha solution” (7:3 concentrated H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) at room temperature for 1 h. *Warning: piranha solution is a highly reactive mixture and severely exothermic during reaction. It should be kept in the hood and away from oxidizable organic materials.* After 1 h exposure in piranha solution, the slides were rinsed

with large amounts of DI water, dried with high purity nitrogen, and dried in an oven for about 1 h at  $\sim 80^\circ\text{C}$  before reacting with alkylchlorosilane.

The glass vials used for the reaction were also cleaned in the same way as the fused-silica slides. After cleaning by the piranha solution, 30 ml hexadecane with a drop of ODS were poured into the dried glass vials for  $\sim 30$  min in order to alkylate the vial surface. The vials were then rinsed thoroughly in the order of hexadecane, toluene, methanol, and acetone, and repeated five times. The vials were finally dried with nitrogen and put in the oven for at least 1 h before use.

### 2.3. Monolayer formation

The rms roughness of the untreated slides was found by AFM to be 1.7 nm. If one assumes a  $A[\sin(2\pi x/\lambda)]^{1/3}$  structure for the surface of the silica with  $A = 2\lambda$ , a rms roughness of 1.7 nm would approximately correspond to a pore diameter of 3 nm. This pore size corresponds to a smaller pore size in commercial use. Each freshly cleaned fused-silica slide was put into the glass vials modified with ODS and immersed with 30 ml anhydrous toluene containing 4 mmol alkylchlorosilane (ODMS, TMS, ODS, or the mixtures of ODMS and TMS). Monolayers that have minimal crosslinking (referred to as “surface-bonded” monolayers) were formed by adding 0.6 ml ethyldiisopropylamine to the solution to promote surface reaction. The adsorbed amine was found to be able to promote covalent bonding between the chlorosilane and the silica surface [8]. It has been found that ODS monolayers prepared in such a way are primarily surface-bonded. After reacting at room temperature for 3 days, the slides were rinsed with toluene, methanol, and acetone. The slides were then dried with high purity nitrogen and stored in sealed plastic vials. Before contact angle measurements and SF spectroscopy experiments, each slide was rinsed with acetone and dried in an oven at  $80^\circ\text{C}$  for 0.5 h.

### 2.4. Contact angle measurements

Contact angles were measured with a Rame-Hart Model 100 goniometer under ambient conditions. For advancing contact angles, an advancing-drop

method was employed and 15 water drops were measured and averaged for each slide. For static contact angles, a drop of liquid was deposited on the slides by a syringe and allowed to equilibrate at least 1 min before reading, and at least five drops were measured and averaged.

### 2.5. Sum-frequency (SF) spectroscopy

The experimental setup for SF spectroscopy is described in detail elsewhere [28]. Briefly, a lithium niobate ( $\text{LiNbO}_3$ ) optical parametric oscillator (OPO) is pumped with a Surelite I (Continuum)  $\text{Nd}^{3+}$ :YAG laser at 1064 nm using relay imaging. Tunable infrared light is generated between 2600 and  $3200\text{ cm}^{-1}$  ( $3.1\text{--}3.8\ \mu\text{m}$ ) with a pulse width of 7 ns. The polarization of the infrared beam is controlled by a Soleil-Babinet compensator and the wavelength is calibrated with a standard polystyrene thin film. The visible light at 532 nm used in the SF experiments is produced by frequency doubling the 1064 nm light in a potassium dihydrogen phosphate (KDP) crystal. SF spectra are obtained by using a total internal reflection geometry. The infrared and visible beams are combined through a coupling prism to the fused silica slide with an index-matching liquid. The generated sum-frequency signal is collected and passed through several collimating optics, absorptive, interference and holographic filters, and a Glan-Taylor polarizer. Signal is detected with a photomultiplier tube and then passed to a preamplifier and gated electronics. Data were collected from  $2800$  to  $3000\text{ cm}^{-1}$  at  $2\text{ cm}^{-1}$  increments, and each data point was the average of 200 laser shots. The sampling size on the surface was determined by the laser spot size which was approximately  $200\ \mu\text{m}$  in diameter. The data are then corrected for the wavelength dependence of the Fresnel factors of the input infrared beam and fit with a Voigt line shape.

## 3. Results and discussion

### 3.1. ODMS monolayers

#### 3.1.1. ODMS monolayers at solid/air interface

Fig. 1(a) shows the SF spectrum of an ODMS

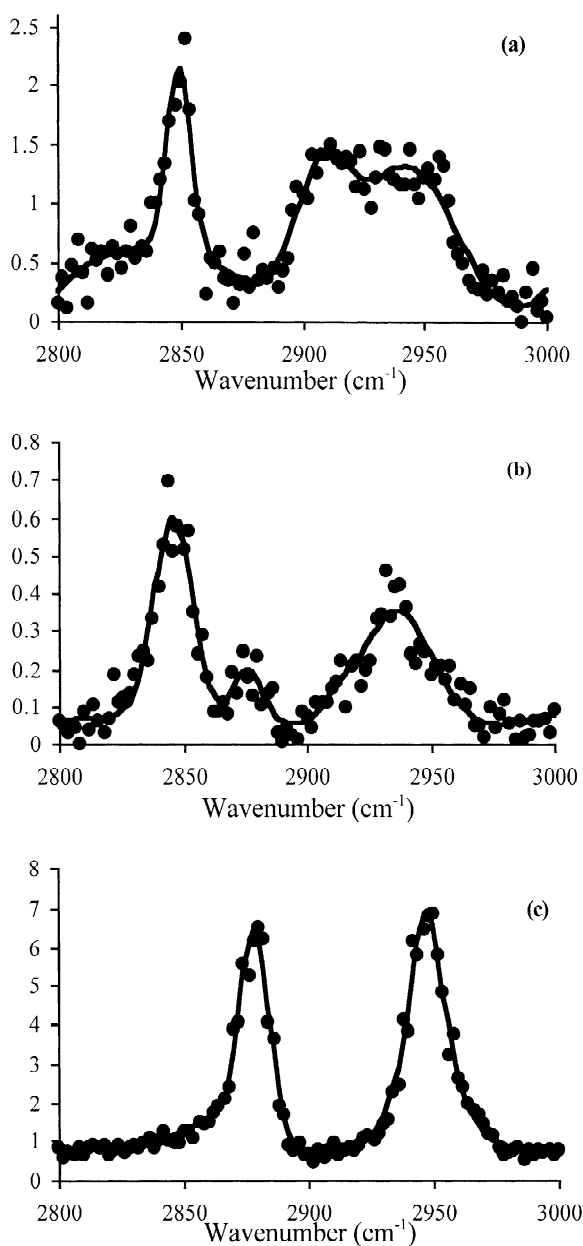


Fig. 1. SF spectra of: (a) ODMS monolayer; (b) surface-bonded ODS monolayer; and (c) highly crosslinked ODS monolayer on fused-silica surface exposed to air. The polarization combination is ssp. (s—polarized SF, s—polarized visible light, and p—polarized infrared light).

modified fused-silica slide exposed to air. The polarization combination for this spectrum is ssp. (s—polarized SF, s—polarized visible light, and p—

polarized infrared light). Three peaks are observed here, with peak positions at  $\sim 2850$ ,  $\sim 2910$  and  $\sim 2950$   $\text{cm}^{-1}$ . By comparing this spectrum with other spectroscopic results [29,30], the three peaks can be assigned to the symmetric stretch of methylene, symmetric stretch of the methyl groups bonded to the silicon atom in the ODMS molecule, and the asymmetric stretch of the methylene group, respectively. One important feature is the strong peak corresponding to the methylene symmetric stretch, which has been successfully used to characterize the carbon chain disorder in a variety of systems. When the long carbon chains are in an all-trans conformation, this vibrational mode is not SF active because of the near complete cancellation of the nonlinear polarization on the adjacent carbon. However, when there are gauche defects in the alkyl chain, the methylene symmetric vibrational mode can be observed in SF spectra due to the change of the local symmetry in the carbon chain. Another feature of this spectrum is the lack of a peak at  $\sim 2875$   $\text{cm}^{-1}$  corresponding to the symmetric stretch of the methyl group on the alkyl chain, which is SF active when the methyl group is normal to the surface. The methyl symmetric stretch observed in this spectrum is shifted to a higher wavenumber than that of the methyl symmetric stretch typically found in alkyl chains ( $2872$ – $2876$   $\text{cm}^{-1}$ ). This peak can be attributed to the side methyl groups bonded directly to the silicon atom, resulting in a shift in energy. From the above discussion, the conformation of alkyl chains in the ODMS monolayer on fused-silica slides can be deduced. As illustrated in Fig. 2(a), the alkyl chains in ODMS are highly disordered and have significant gauche content, with the methyl group on the alkyl chains mainly oriented away from the surface normal (confirmed by sps. spectra, not shown). This result is in agreement with the work of Sander et al. [31] and Pemberton et al. [32,33], who used IR or Raman spectroscopy to study the alkyl chain conformation in the stationary phase modified with ODMS. Both found that the stationary phase alkyl chains existed in a highly disordered, liquid-like state on the silica surfaces of the packing materials.

The highly disordered alkyl chain for ODMS modified fused-silica surface is quite different from that of a monolayer of highly crosslinked ODS where significant all-trans conformation is observed

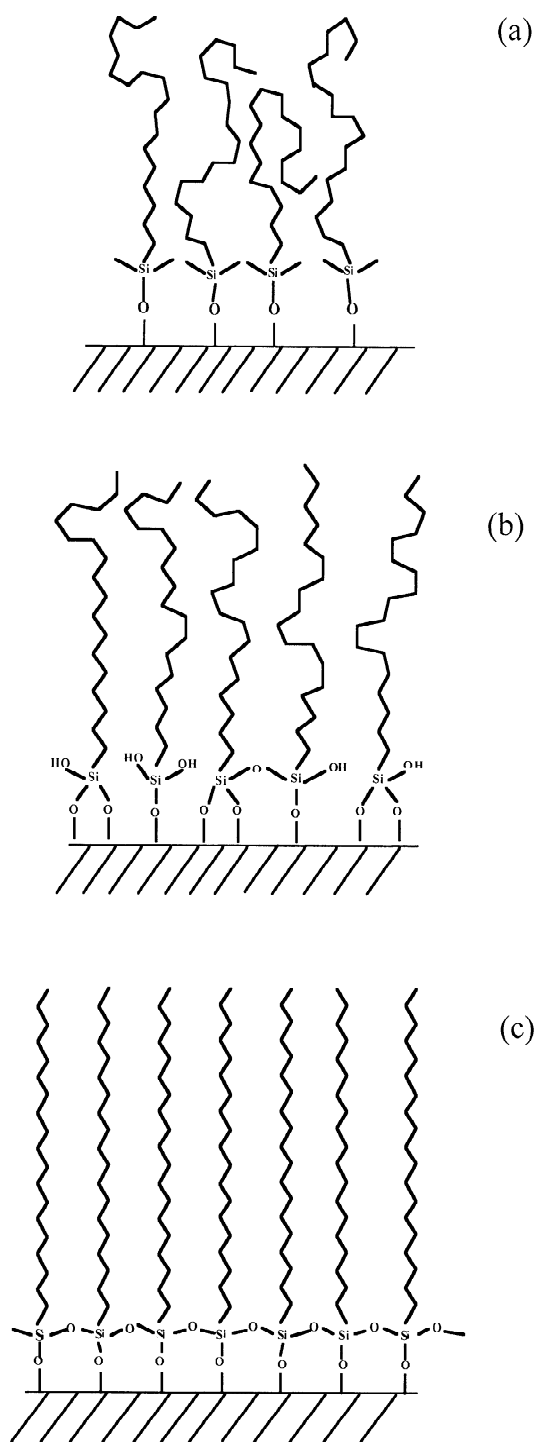


Fig. 2. Proposed conformations of: (a) ODMS monolayer; (b) surface-bonded ODS monolayer; and (c) highly cross-linked ODS monolayer on fused-silica substrates.

and the average orientation of the methyl group in the alkyl chain is primarily normal to the surface [29,30]. It is not surprising when one considers the difference in the structures and the reaction mechanisms between ODS and ODMS. In forming the ODS monolayer, the precursor OTS molecule has three hydrolyzable groups and the molecules can cross-link to each other, forming a highly crosslinked monolayer on the surface. The typical Si–O bond length is about 1.6 Å, and the length of the Si–O–Si cross-link is usually shorter than twice that of the Si–O bond length [34]. Therefore, the ODS monolayer is very closely packed [34]. According to previous work, the cross-sectional area of ODS is around 20 Å<sup>2</sup>, which corresponds to a surface density for the ODS monolayers of about 8 μmol/m<sup>2</sup> [8,35]. Consequently, the alkyl chains become highly oriented to maximize van der Waal's interactions. In the case of ODMS monolayers formed from monofunctional octadecyl dimethyl silane, there is only one hydrolyzable group so no crosslinking can occur once surface bonding has occurred. In addition, there are two bulky methyl groups on the Si atom. The cross-sectional area of ODMS was calculated to be ~32–38 Å<sup>2</sup>, corresponding to a maximum possible coverage of ~4.5 μmol/m<sup>2</sup> [8,35] which is almost half of that for ODS. As a result, the ODMS molecules are less tightly packed on the surface and the van der Waals chain–chain interactions are much smaller than that of close-packed ODS monolayer. In addition, there is more area for the alkyl chain in the ODMS monolayer allowing it to assume a more disordered conformation.

In order to determine whether the observed disorder in ODMS is due to steric effects of the silicon bonded methyl groups or the lack of crosslinking, “surface-bonded” and “highly crosslinked” ODS were studied and compared with ODMS. The SF spectrum of surface-bonded ODS and highly crosslinked ODS are shown in Fig. 1(b) and (c), respectively. A small peak at ~2875 cm<sup>-1</sup> corresponding to the symmetric stretch of methyl group is observed in Fig. 1(b), indicating that unlike in ODMS monolayers, the alkyl chains in surface-bonded ODS are more ordered. Though this monolayer may appear more ordered, the strong peak due to the methylene symmetric stretch shows that like ODMS, the alkyl chain still has a significant amount of gauche con-

tent. In contrast, the spectrum in Fig. 1(c) of highly crosslinked ODS shows a dramatically different conformation. The two peaks at 2875 and 2950  $\text{cm}^{-1}$  are the classic methyl symmetric stretch and Fermi resonance observed in very well ordered monolayers. The conformation of surface-bonded ODS and highly crosslinked ODS are illustrated in Fig. 2(b) and (c), respectively. The different conformations of surface-bonded and highly crosslinked ODS monolayers indicate that the chain disorder in ODMS is probably controlled by the lack of crosslinking between the ODMS molecules, rather than steric effects of the methyl side groups.

Water advancing contact angles measured for the ODMS and the surface-bonded ODS are 104 and 102°, both similar to the reported values in the literature [8,19]. If we treat the modified fused-silica surfaces as a mixture of methyl and methylene surfaces, the contribution of the two groups to the wettability can be evaluated from Israelachvili-Gee equation [36]:

$$(1 + \cos \theta)^2 = f_1 (1 + \cos \theta_1)^2 + f_2 (1 + \cos \theta_2)^2$$

where  $\theta$  is the contact angle of heterogeneous surfaces,  $\theta_1$ ,  $\theta_2$  are the contact angles of pure surfaces,  $f_1$  and  $f_2$  are the fractional areas occupied by the two components, and  $f_1 + f_2 = 1$ . This equation is used instead of the Cassie equation since the latter does not take into account the microscale surface heterogeneity, especially for surfaces modified with thin films [36]. The water contact angles for pure methyl and methylene surfaces are assumed to be 110 and 94°, respectively [19]. The water contact angle on a highly crosslinked ODS monolayer is 110° and is equal to that of the pure methylated surface, indicating that water only interacts with the methyl groups and does not penetrate into the monolayer or interact with residual silanol groups on the silica surface. For the ODMS monolayer that exhibits a lower contact angle, Eq. (1) can be used to estimate the surface composition and therefore the alkyl chain conformation. According to Eq. (1), water interacts with 70% methyl and 30% methylene groups in the ODMS monolayer, and 55% methyl and 45% methylene groups in surface-bonded ODS. The smaller interactions with methyl groups could also be due to interactions with residual

silanols, which will be more exposed in the surface-bonded ODS monolayer. Since the ODMS surface has two types of methyl groups, one cannot deduce the relative surface conformation from these data.

### 3.1.2. ODMS monolayers at the solid/acetonitrile and solid/water interfaces

Fig. 3 shows the SF spectra (ssp polarization combination) of ODMS monolayers on a fused-silica substrate in contact with water and acetonitrile. Similar to the solid/air interface, in both solvent environments only the symmetric stretch of the methylene group, the symmetric stretch of the methyl groups bonded to the silicon atom, and the asymmetric stretch of the methylene group were detected. There is a slight red shift in both the asymmetric stretch of methylene (2950  $\text{cm}^{-1}$ ) and the symmetric stretch of methyl (2910  $\text{cm}^{-1}$ ) going from water to an acetonitrile environment due to the change in solvent polarity. The shift is significant yet quite small ( $<4 \text{ cm}^{-1}$ ) and is within the resolution of our instrument. The observed symmetric stretch of the methylene groups and the lack of the symmetric vibrational mode of the methyl group again indicate that the ODMS monolayer has a high degree of disorder and there appears to be little solvent-induced conformation change. However, the reason for the lack of significant solvent-induced conformational change is different from that of the highly crosslinked ODS, since the packing density of

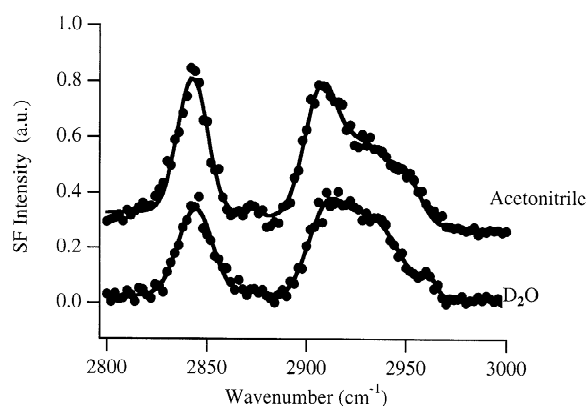


Fig. 3. SF spectra of an ODMS monolayer on a fused-silica substrate in contact with water and acetonitrile. The polarization combination is ssp. (s—polarized SF, s—polarized visible light, and p—polarized infrared light).

ODMS is almost half of that of the ODS. It may be because the ODMS monolayer is so disordered that the solvent cannot penetrate into the alkyl chain and hence change the alkyl chain order.

As mentioned previously, there is no solvent-induced conformational change for close-packed highly crosslinked ODS monolayers on fused-silica. Thompson [23] used Raman spectroscopy to study ODS on a  $\text{SiO}_2/\text{Ag}$  substrate and found that the alkyl chains were not disrupted when contacted with acetonitrile and water. SF spectroscopy studies in our group [24] also showed that for highly crosslinked ODS monolayers on fused-silica surface, no methylene symmetric stretch was observed both in water and acetonitrile. However, distinct from the ODMS monolayer, the lack of solvent induced monolayer disorder in ODS was attributed to the higher packing density on the fused-silica substrate than that on silica gel particles. In densely packed monolayers, sufficient surface area was not available for increased chain disorder to occur.

### 3.2. ODMS/TMS mixed monolayer

Fig. 4 shows the SF spectra of mixed ODMS and TMS monolayers on fused-silica exposed to water and acetonitrile solvent. The strong peak  $\sim 2910\text{ cm}^{-1}$  for TMS monolayer results from the methyl symmetric stretch peak and the small peak at  $\sim 2965\text{ cm}^{-1}$  results from the methyl asymmetric stretch vibration. In both solvents, the ratio of the peak area of the symmetric stretch of the methylene to the symmetric stretch of the methyl groups bonded to the silicon atom decreases with the decreasing ODMS fraction. When the ODMS fraction is 93% (the fraction in the preparation solution), the methylene symmetric stretch is barely observed. This may be because the alkyl chain is randomly ordered so that it cannot be detected by SF spectroscopy. As can be seen in the spectra, there are slight differences in monolayers in contact with water and acetonitrile in the region between 2920 and 2970  $\text{cm}^{-1}$ . In  $\text{D}_2\text{O}$ , the asymmetric stretch of the methylene group at  $2950\text{ cm}^{-1}$  has a higher intensity than in acetonitrile. This high intensity makes it difficult to discern a shift in peak position with solvent environment since this peak overlaps the methyl peak originating from TMS. Overall, slight effects of solvent can be

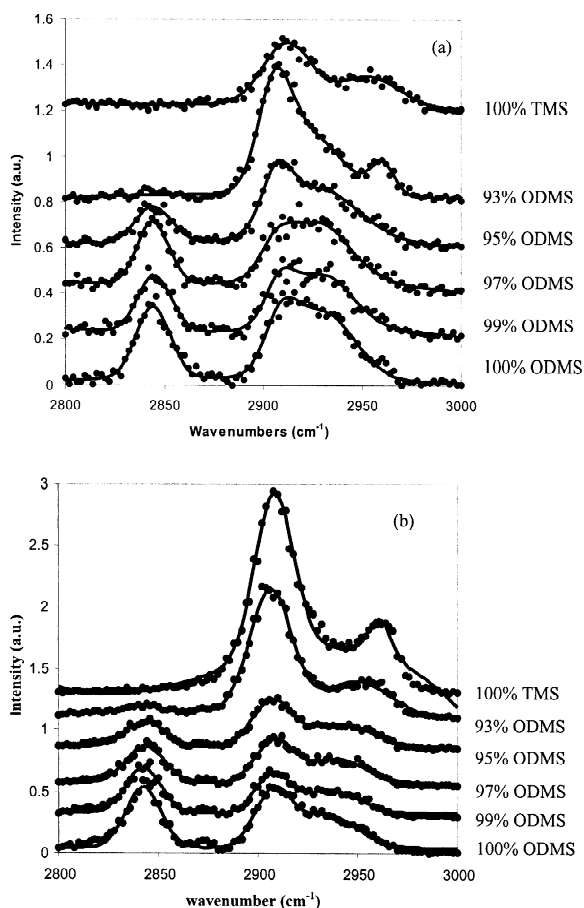


Fig. 4. SF spectra of ODMS-TMS mixed monolayers on fused-silica substrate in contact with (a) 100% water and (b) 100% acetonitrile. The polarization combination is ssp.

observed on the structure of the monolayer, but no large solvent effects are found, indicating that unlike ODS/MS mixed monolayer [24], the ODMS/TMS mixed monolayer is not sensitive to the change in solvent environment. This result is consistent with an absorptive mechanism and the recent work of Pemberton et al. that found that polar solvents do not significantly intercalate into the stationary phase [37].

The advancing water contact angles measured for 100% ODMS, 99% ODMS, 97% ODMS, 95% ODMS, 93% ODMS and 100% TMS are listed in Table 1. TMS has three methyl groups, but the water contact angle is smallest. This is because water can penetrate into the monolayer due to the short alkyl



Table 1  
Advancing water contact angles for ODS/CTMS mixed monolayer

Composition	100% ODS	99% ODS	97% ODS	95% ODS	93% ODS	100% CTMS
Contact angle	104°	106°	106°	104°	99°	95°

chain length and interact with the silanols on the substrate surface. The lack of crosslinking prevents the formation of a tightly packed monolayer. For ODMS fractions greater than 95%, the water contact angle does not change significantly, indicating that the alkyl chain is so disordered that the water can not intercalate into the monolayer and only interacts with the methyl and methylene groups. The smaller water contact angle for 93% ODMS indicates that water can penetrate into the mixed monolayer due to the lower ODMS packing density.

#### 4. Conclusions

ODMS, ODMS/TMS mixed monolayers and ODS monolayers on fused-silica were studied by SF spectroscopy and contact angle measurements. Examination of the different conformations of surface-bonded and highly crosslinked ODS monolayers indicate that the chain disorder in ODMS is probably controlled by the lack of crosslinking between the ODMS molecules, rather than steric effects of the methyl side groups. The alkyl chains in the ODMS and the ODMS/TMS monolayers are highly disordered and are weakly sensitive to the change in solvent environment due to low packing density and small van der Waals chain–chain interactions. Calculations using contact angle data on ODMS monolayers showed that water interacts 70% with methyl groups and 30% with methylene groups. Furthermore, at ODMS fractions greater than 95%, water cannot penetrate into the monolayer possibly because of the high degree of disorder. However, at ODMS fractions lower than 95%, water is able to penetrate into the monolayers and interact with the substrate.

#### Acknowledgements

The authors gratefully acknowledge support from the National Science Foundation (CHE-9875632).

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