

# Chain Conformation of Poly(dimethyl siloxane) at the Air/Water Interface by Sum Frequency Generation

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This is to report a study of chain conformation of poly(dimethylsiloxane) (PDMS) in spread monolayers at the air/water interface (A/W) with the aid of vibrational sum frequency spectroscopy (VSFS). We find that methyl groups of PDMS chains at the interface are completely disordered in the dilute regime of the surface density. At higher surface densities, however, the two methyl groups on the repeating unit point into the air asymmetrically; one points more normal to the interface, whereas the other lies more parallel to the interface. In the first collapsed regime, where the surface pressure of the PDMS monolayer reaches a plateau value of 8.7 mN/m, the signal intensity at 2915 cm<sup>-1</sup>, assigned to the symmetric vibrational frequency of the methyl groups, is found independent of the surface density. On the basis of this finding, we propose that PDMS chains, in the first collapse regime at the A/W, form asymmetric layers. Thus, our proposal lends support to earlier works by Langevin's group to refute a widely speculated helix model that was based on energy minimization in the crystalline state of PDMS. In short, the energy consideration in the bulk crystalline state does not provide meaningful guidance as to the chain conformation of the monolayer at the A/W.

## Introduction

Poly(dimethylsiloxane) (PDMS) is the central pillar of siloxane polymers.<sup>1,2</sup> It exhibits distinctive properties over those of hydrocarbon polymers. Its surface tension is lower than most other polymers except those based on aliphatic fluorocarbon moieties. Its glass transition temperature of -123 °C is among the lowest for polymers; moreover, its excellent thermal and oxidative stability confers an added factor for its wide commercial applications. The chemical structure of this heteroatom backbone, accounting for these unique properties, is shown in Figure 1a. Attributed to this structure are the following features: low intermolecular force between methyl groups, very flexible backbone, high Si-O bond energy, and partial ionic character of the bond. What interests us the most is the versatile surface properties<sup>3</sup> of PDMS such that the hydrophilic Si-O backbone along with hydrophobic methyl pendent groups confers surface activity at the air/water interface (A/W).

Monolayer studies of PDMS at the A/W were first reported by Fox et al. 60 years ago.<sup>4</sup> Since then, they abound in the literature ensuing reports.<sup>5-14</sup> Interest, of course, resides in the enormous technological importance of this polymer, spanning

over the past three-quarters of a century. In the report by Fox et al., an intriguing surface pressure isotherm was presented, as shown in Figure 2, which has subsequently been reproduced repeatedly. Historically, a model based on the molecular structure, as displayed in Figure 3, was put forth to provide a rationale for the "transitions" noted in the isotherm relative to surface density, while more recent works<sup>10,12,13</sup> by Langevin's laboratory have challenged its veracity; we should note here that the term "surface concentration" is often used interchangeably with "surface density". Their descriptions of the chain conformations are as follows:<sup>4</sup> In the low surface concentration regime (regime A), polymer chains are uncoiled on the surface, i.e., they adopt a "flat" conformation with both silicon and oxygen atoms immersed into the water subphase. As the surface concentration increases, the surface pressure starts to build up (regime B), and some of the silicon and oxygen atoms are pushed out of the interface. Further compression of the film (regime C) leads to the first "collapse" with a constant surface pressure value at 8.7 mN/m, which is ascribed to successive coiling of polymer chains into a helical conformation. The 6/1 helix structure was confirmed to be the lowest energy conformation in the crystalline state of PDMS,<sup>5</sup> while a more extended helical structure was suggested by a solid-state NMR study.<sup>6</sup> In the most concentrated regime D, after a modest increase in surface pressure from regime C, a second plateau in the surface pressure is reached, which is attributed to conformational changes to upright helices. An alternative molecular model, appearing between 1963 and 1971, proposed by Noll et al.,<sup>7-9</sup> involves hydration of the polymer backbone and squeezing-out of water when the film is compressed for the early stages of the isotherm.

Besides these isotherm studies, two-dimensional phase behavior of the PDMS films has been examined. A Brewster angle microscopic study<sup>10</sup> showed surface heterogeneity in the most dilute and the most concentrated concentration regimes (A and

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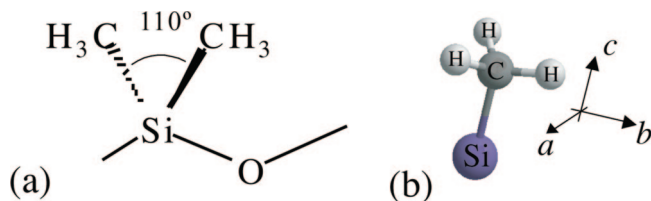
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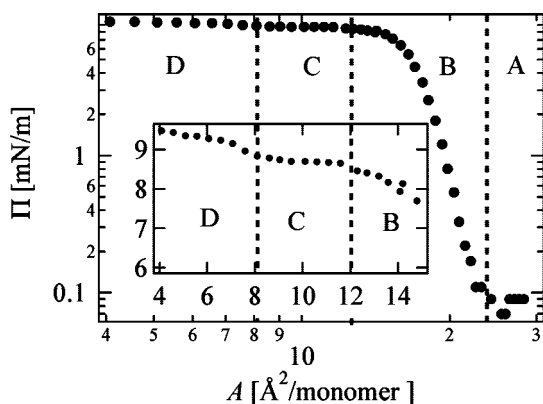
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**Figure 1.** (a) Chemical structure of PDMS and (b) molecular coordinates of the methyl group.

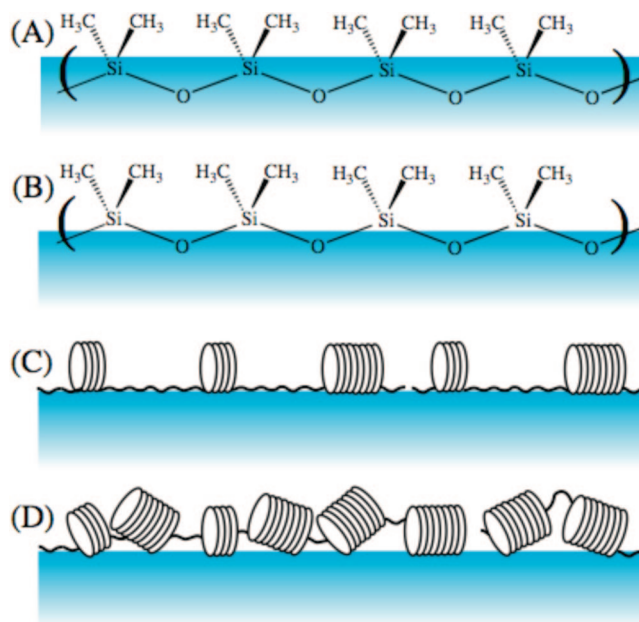


**Figure 2.** Surface pressure–area isotherm of PDMS monolayer at room temperature. Surface concentrations, the inverse of area/monomer, are purposely demarcated into four regions, A–D, corresponding to distinctive  $\Pi$ – $A$  characteristics.<sup>14</sup>

D), and fluorescence microscopic studies<sup>11</sup> suggested a patchy-island structure in the first plateau regime (C). In the same study, reflectance infrared analysis also suggested the helix formation in this first “collapse” plateau (C). Lee et al.<sup>12</sup> and Mann and Langevin<sup>13</sup> made the attempts to reexamine the chain conformation of PDMS films using the techniques of high-resolution ellipsometry and neutron reflectivity. They concluded that the conformational changes at the A/W are not as smooth and progressive as suggested in the earlier models, and the formation of bilayers and multilayers is likely as opposed to regular helical conformation. These studies, however, suffer from what we regard as the limits of the techniques involved. First, the ellipsometry cannot decouple the mass density from the film height, and, second, the neutron reflectivity employed a rather limited range of momentum transfer, 0–0.02 Å<sup>−1</sup>, to produce detailed profiles of film density and height as a function of surface density.

A more detailed neutron reflectivity study<sup>14</sup> showed that PDMS monolayers in regimes A and B contain about 30% water by volume, and they are thicker than the model by Fox et al.<sup>4</sup> Inferred from these results, it has been suggested that PDMS chains might not uncoil completely to adopt ideal random conformation on the surface but form loose helical turns. Also, the chain conformational change corresponding to the thickness plateau was attributed to compressing loose helical turns to dense helices and squeezing water out of monolayers through a dehydration process, resulting in increased density under a constant thickness. However, to our knowledge, there has been no direct evidence to confirm the proposed models, and the chain conformation models in the monolayer at the A/W are yet to be validated directly.

A promising new technique to address these open questions for the chain conformation could be vibrational sum frequency spectroscopy (VSFS). It relies on a second-order nonlinear optical process, which is forbidden in a bulk medium that possesses



**Figure 3.** Proposed conformational changes in PDMS isotherms at the A/W. The regions correspond to (A) all Si and O atoms adsorbed onto the interface, (B) some of the Si and O atoms adsorbed (drawn as only O adsorbed for convenience), (C) helices with their axis parallel to the surface, and (D) helices oriented more perpendicular to the interface.<sup>4</sup>

inversion symmetry in the transition dipole moment; hence, this technique is highly surface-specific where the inversion symmetry is broken.<sup>15</sup> VSFS has been applied to the investigation of monolayers of simple surfactants at the A/W<sup>16–20</sup> and the chain orientation of polymers at the air/polymer interface and water/polymer interface.<sup>21–24</sup>

The aim of this study is to investigate the chain conformation of PDMS monolayers at the A/W using the VSFS method, with an expectation that this technique should provide us with a means to shed better light on the issue. Orientation of the methyl groups is evaluated with the VSF spectra of the PDMS monolayer in the C–H stretching vibrational region. The conformation of PDMS polymer chains at the interface is inferred from the orientation of the methyl groups.

## Experimental Section

**Materials and Monolayer Preparation.** Deionized water without any specific buffering is used as the subphase. The deionized water is further purified by a NANOpure Ultrapure Water system (Barnstead, Dubuque, IA) with a minimum resistivity of 18 MΩ at the outlet. The PDMS sample, having a number average molecular weight of 10,060 g/mol and a polydispersity index of 1.15, was a

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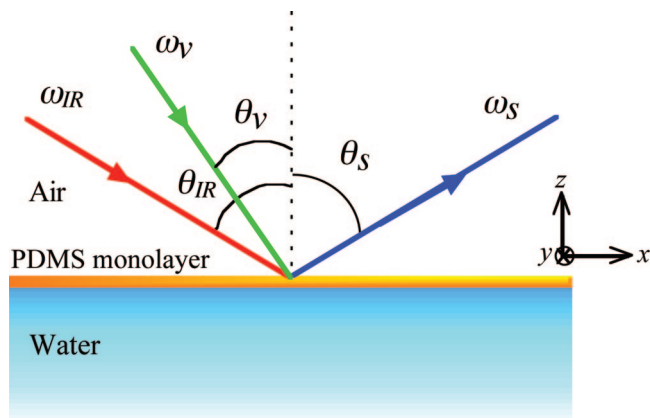
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**Figure 4.** Schematic experimental setup for VSFS on a PDMS monolayer at the A/W.

generous gift of Prof. S. J. Clarson of Cincinnati.<sup>7,25</sup> HPLC-grade chloroform was purchased from Aldrich and is used as a spreading solvent without further purification. A PDMS solution with a concentration of 0.027 g/L is prepared in chloroform. The area per monomer, which is the inverse of the surface concentration, is varied from 29.4 to 2.5 Å<sup>2</sup>/monomer by successive additions with a substantial waiting period to reach apparent equilibrium for each addition.

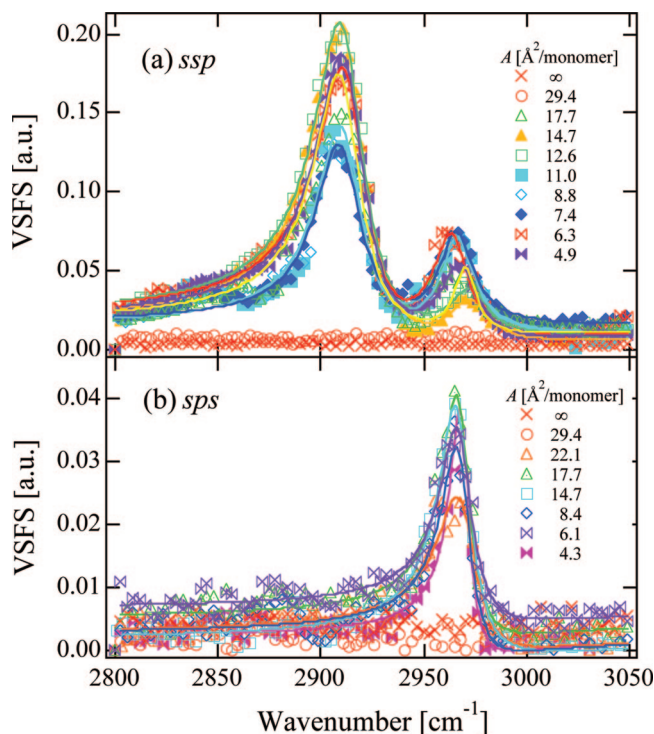
**VSFS.** A beam of 1064 nm in a wavelength from a mode-locked Nd:YAG laser (PY61c, Continuum, Santa Clara, CA), operated at a 20 Hz repetition rate with a peak width of 21 ps, is used to pump an optical parametric generation/amplification (OPG/OPA) stage (Laser Vision, Bellevue, WA) to produce a tunable IR beam from 2800 to 3100 cm<sup>-1</sup> in addition to a frequency doubled beam at 532 nm.<sup>26</sup> In Figure 4 is displayed a schematic diagram of the experimental setup. The IR and the visible beams were overlapped at the A/W with incident angles of 51° and 42°, respectively, relative to the surface normal.

Here, we present a brief overview of the background of VSFS for the sake of completeness and in the context of PDMS structure, while theoretical details are deferred to the extensive literature.<sup>18,19,24,27</sup> Sum frequency signal intensity,  $I_{\text{SF}}$ , is proportional to the square of the second-order nonlinear susceptibility,  $\chi^{(2)}$ . The corresponding susceptibility tensor can be described by a frequency-dependent resonant term,  $\chi_{\text{R}}^{(2)}$ , and a frequency-independent non-resonant term,  $\chi_{\text{NR}}^{(2)}$ . The intensity of the sum frequency signal can be written as

$$I_{\text{SF}} \propto |\chi^{(2)}|^2 I_{\text{IR}} I_{\text{VIS}} \quad (1)$$

$$\chi^{(2)} = \chi_{\text{NR}}^{(2)} + \chi_{\text{R}}^{(2)} = \chi_{\text{NR}}^{(2)} + \sum_n \frac{A_n}{\omega_{\text{IR}} - \omega_n + i\Gamma_n} \quad (2)$$

where  $I_{\text{VIS}}$  and  $I_{\text{IR}}$  are intensities of the input visible and infrared beams, respectively.  $A_n$  is the oscillator strength of the  $n$ th resonant mode that includes the density of oscillators, their orientational vector average, and the strength of the IR and Raman transition moments. In eq 2, the symbols  $\omega_{\text{IR}}$ ,  $\omega_n$ , and  $\Gamma_n$  represent, respectively, the frequency of the incoming IR beam, the frequency of the  $n$ th resonant mode, and its peak width. All spectra in this study are taken with two polarization combinations; “ssp” and “sps”, where the three characters represent the polarization directions of the sum frequency, visible, and infrared beams, respectively. The symbol  $p$  stands for the parallel polarization to the incident plane, whereas  $s$  stands for the perpendicular polarization. Each data set is normalized to a



**Figure 5.** VSFS Spectra of (a) ssp and (b) sps polarization combinations from PDMS monolayer at the various surface concentrations.

spectrum taken from a piece of Y-cut crystalline quartz. Data are fitted with a Voigt profile to yield the oscillator strength of individual resonances. This takes into account both homogeneous and inhomogeneous line broadening.

More specifically for PDMS, the orientation of methyl groups can be determined by relating the macroscopic second-order nonlinear susceptibility tensor  $\chi^{(2)}$  to the molecular hyperpolarizability tensor  $\alpha^{(2)}$ .<sup>23</sup> Methyl groups will be assumed to have  $C_{3v}$  symmetry.<sup>28</sup> By taking a ratio of the magnitude of the nonlinear susceptibility of the two methyl groups in the asymmetric (as) and the symmetric (s) modes in the same polarization, we can conveniently eliminate the effect of the Fresnel factors, refractive indices, and incident angles of the input beams and get the following two equations:

$$\left| \frac{\chi_{\text{yyz,as}}}{\chi_{\text{yyz,s}}} \right| = \left| \frac{\chi_{\text{ssp,as}}}{\chi_{\text{ssp,s}}} \right| = \left| \frac{2\alpha_{\text{caa}}[\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle]}{\alpha_{\text{caa}}[\langle \cos \theta \rangle (1+r) - \langle \cos^3 \theta \rangle (1-r)]} \right| \quad (3)$$

$$\left| \frac{\chi_{\text{zyz,s}}}{\chi_{\text{zyz,as}}} \right| = \left| \frac{\chi_{\text{sps,s}}}{\chi_{\text{sps,as}}} \right| = \left| \frac{\alpha_{\text{ccc}}[\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle] (1-r)}{\alpha_{\text{acc}} \langle \cos^3 \theta \rangle} \right| \quad (4)$$

Here,  $x$ ,  $y$ , and  $z$  are the laboratory coordinates where the  $x$  axis is in the incident plane, the  $y$  axis is normal to the incident plane, and the  $z$  axis is along the interface normal, as shown in Figure 4, while  $a$ ,  $b$ , and  $c$  are molecular axes where the  $c$  axis is chosen to coincide with the symmetry axis of a methyl group and the other two axes are perpendicular to the axis  $c$  and are assumed to have a random spatial distribution, as illustrated in Figure 1b. Also,  $r$  is defined as  $r = \alpha_{\text{aac}}/\alpha_{\text{ccc}}$ , and it can be assumed that  $\alpha_{\text{aac}} \approx -\alpha_{\text{caa}}$  for the methyl group vibration.<sup>29</sup> We may also assume that the bond angle of the two methyl groups on the Si atom always maintain 110°, as shown Figure 1. Hence, we can make the approximations that  $\langle \cos \theta \rangle \approx (\langle \cos \theta_1 \rangle + \langle \cos \theta_2 \rangle)/2$  and  $\langle \cos^3 \theta \rangle \approx (\langle \cos^3 \theta_1 \rangle + \langle \cos^3 \theta_2 \rangle)/2$ ,

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**Table 1. Fitting parameters of *ssp* VSFS Spectra for the Methyl Group of PDMS on an A/W<sup>a</sup>**

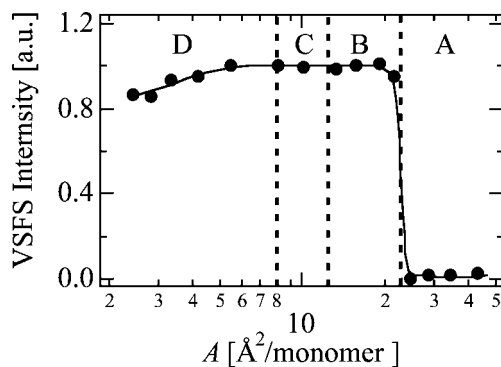
$A$ [ $\text{\AA}^2/\text{monomer}$ ]	$\omega_{ssp,s}$ [ $\text{cm}^{-1}$ ]	$ A_{ssp,s} $	$\Gamma_{ssp,s}$ [ $\text{cm}^{-1}$ ]	$\omega_{ssp,as}$ [ $\text{cm}^{-1}$ ]	$ A_{ssp,as} $	$\Gamma_{ssp,as}$ [ $\text{cm}^{-1}$ ]
17.7	2910.7	$4.2 \pm 0.1$	$13.8 \pm 0.4$	2970.6	$0.8 \pm 0.1$	$6.2 \pm 1.0$
14.7	2911.9	$5.2 \pm 0.1$	$14.4 \pm 0.3$	2973.0	$1.1 \pm 0.2$	$11.5 \pm 2.2$
12.6	2911.9	$4.9 \pm 0.1$	$14.5 \pm 0.3$	2973.1	$1.0 \pm 0.2$	$11.2 \pm 1.9$
11.0	2911.3	$3.4 \pm 0.1$	$13.2 \pm 0.4$	2966.7	$1.5 \pm 0.2$	$9.8 \pm 1.0$
8.8	2911.6	$3.3 \pm 0.1$	$13.7 \pm 0.6$	2965.5	$1.7 \pm 0.2$	$11.1 \pm 1.1$
7.4	2909.8	$3.0 \pm 0.1$	$13.3 \pm 0.6$	2965.4	$1.3 \pm 0.1$	$9.8 \pm 0.9$
6.3	2913.7	$4.2 \pm 0.1$	$14.2 \pm 0.5$	2964.1	$1.8 \pm 0.2$	$10.7 \pm 0.9$
4.9	2912.9	$4.5 \pm 0.1$	$14.1 \pm 0.4$	2968.0	$1.4 \pm 0.1$	$10.8 \pm 1.1$

<sup>a</sup> The subscript “s” is for the CH<sub>3</sub> symmetric vibrational mode, and “as” is for the CH<sub>3</sub> asymmetric vibrational mode.  $A_n$  is the oscillator strength of the  $n$ th resonant mode,  $\omega_n$  is the frequency of the  $n$ th resonant mode, and  $\Gamma_n$  represents its peak width. The standard deviations of  $\omega_n$  are less than  $1 \text{ cm}^{-1}$ , and those for the others are listed in the table.

**Table 2. Fitting Parameters of *sps* VSFS Spectra for the Methyl Group of PDMS on an A/W<sup>a</sup>**

$A$ [ $\text{\AA}^2/\text{monomer}$ ]	$\omega_{sps,as}$ [ $\text{cm}^{-1}$ ]	$ A_{sps,as} $	$\Gamma_{sps,as}$ [ $\text{cm}^{-1}$ ]
29.4	2952.6	$0.8 \pm 1.2$	$11 \pm 1.5$
22.1	2969.3	$1.5 \pm 0.1$	$11.2 \pm 0.9$
17.7	2967.7	$2.1 \pm 0.1$	$8.2 \pm 0.4$
14.7	2967.1	$1.9 \pm 0.6$	$9.6 \pm 0.3$
8.4	2968.1	$1.5 \pm 1.4$	$8.5 \pm 0.5$
6.1	2967.8	$1.1 \pm 0.1$	$9.4 \pm 0.5$
4.3	2968.7	$1.1 \pm 0.5$	$5.7 \pm 0.6$

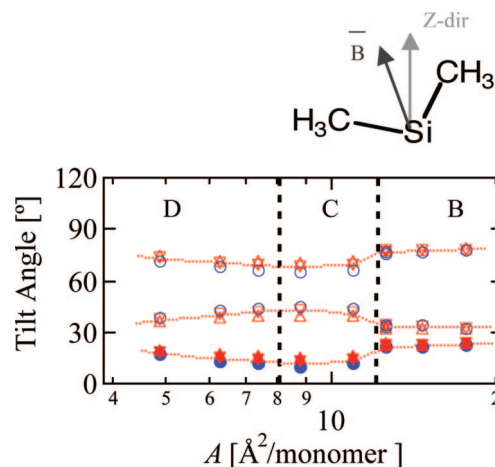
<sup>a</sup> The subscript “as” is for the CH<sub>3</sub> asymmetric vibrational mode.

**Figure 6.** VSFS intensity of *ssp* polarization at  $2915 \text{ cm}^{-1}$  as a function of surface area per monomer.

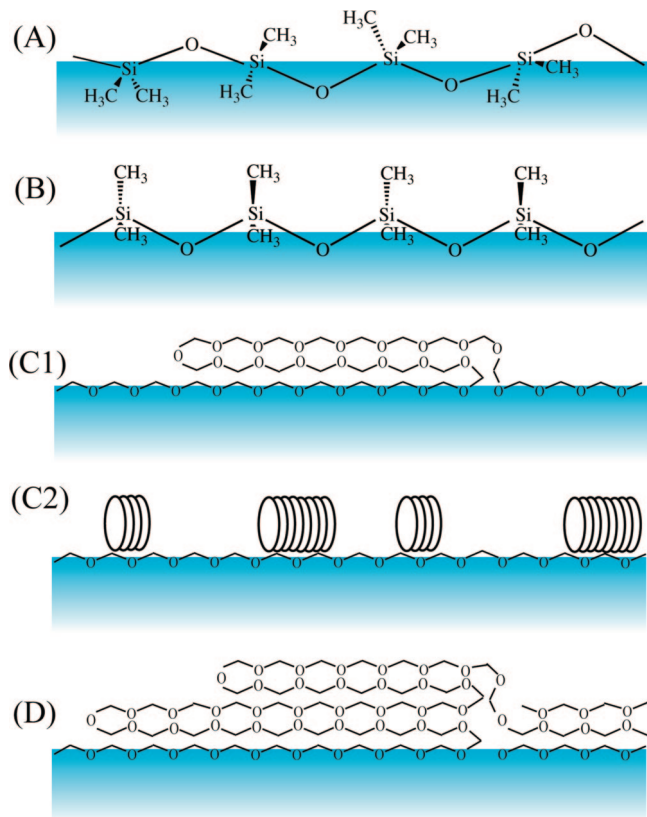
where  $\theta_1$  and  $\theta_2$  are the tilt angles of two methyl groups.  $\langle \cos \theta_2 \rangle$  and  $\langle \cos^3 \theta_2 \rangle$  are obtained by averaging over all possible  $\theta_2 - 110^\circ$  from the first tilt angle,  $\theta_1$ . Then, we can estimate the average orientations of the two methyl groups,  $\langle \theta_1 \rangle \approx \arccos(\langle \cos \theta_1 \rangle)$  and  $\langle \theta_2 \rangle \approx 110^\circ - \langle \theta_1 \rangle$ , from VSFS spectra because now we have two equations and two unknowns, namely  $r$  and  $\langle \theta_1 \rangle$  for eqs 3 and 4.

## Results and Discussions

First, we show in Figure 5 the VSF spectra of PDMS monolayers at various surface concentrations taken in the range of  $2800\text{--}3050 \text{ cm}^{-1}$  with the *ssp* (a) and *sps* (b) polarization combination. Solid curves are fits with eq 2, and the fitting parameters are listed in Tables 1 and 2. Although the oscillator strength values may appear to be randomly fluctuating with the surface concentration change of the polymer, the more important parameter is the ratio between the values, as we explained in the previous section. The most distinctive feature in Figure 5a for the *ssp* polarization is that the VSFS signal from methyl groups at  $2915 \text{ cm}^{-1}$  is undetectable in the dilute regime (regime A), whereas it appears dramatically as the surface concentration crosses into the semidilute regime (regime B). To see this more clearly, we fix the detector at  $2915 \text{ cm}^{-1}$  and keep track of the VSFS intensity as a function of surface concentration at the *ssp* polarization combination. In Figure 6 is displayed how the VSFS intensity gives a sharp rise upon crossing the boundary of A–B and remains constant for the entire range of regime B.

**Figure 7.** Average orientation of the methyl groups in PDMS on an A/W as a function of surface concentration with three different values of  $r = \alpha_{\text{as}}/\alpha_{\text{cc}}$  (circles:  $r = 1.0$ , lower triangles:  $r = 1.6$ , and upper triangles:  $r = 4.8$ ). Open symbols are for the each methyl group separated by  $110^\circ$ , and filled ones are for the angle between the surface normal and the vector ( $\vec{B}$ ) bisecting the C–Si–C plane from Si. The dotted lines are to guide the eye.

We turn briefly to interpret this finding. An inference is drawn that the methyl groups of PDMS in regime A (dilute concentration) do not point outward to the air phase as in the earlier conjecture (Figure 3A). Instead, there are two possible conformations to account for the results. In the first, the methyl groups are totally random-oriented, and in the other they are plane-symmetric to the interface, i.e., in the plane of the  $x$ – $z$  axis, such that one methyl group points out into the air and the other points into the water. However, the second possibility is less likely since it imposes asymmetry of the environment for the hydrophobic methyl group. More likely, as in the first possible conformation, the orientation of methyl groups is totally random and the PDMS chains are completely disordered as freely rotating in the regime A. There are a couple of experimental results lending support to this possibility. First, they are determinations of the monolayer thickness by neutron reflectometry measurements.<sup>14</sup> They showed the thickness of PDMS monolayers even in the dilute regime to be about  $15 \text{ \AA}$ ; this is twice as thick as a single molecular layer



**Figure 8.** Modified chain conformation model of PDMS isotherms at the A/W. The regions correspond to the same concentration as in Figure 4: (A) randomly rotating chains, (B) monolayers with one methyl group close to the surface normal and the other to the surface, (C) monolayers mixed with horizontal folding layers, and (D) horizontally folding multilayers. O refers to oxygen atom. Other atoms are not explicitly shown for the sake of clarity.

thickness of 6 Å. The others are surface potential measurements of the monolayer that show a similar sharp rise at the boundary of A–B from 0 mV to 200 mV, and remains constant at 200 mV for the entire range of regime B.<sup>30–32</sup>

Now, we move on to the results obtained in higher surface concentrations beyond regime A. The VSF spectra of the *ssp* polarization (Figure 5a), show two dominant peaks at 2910 and 2965  $\text{cm}^{-1}$  corresponding to the symmetric and asymmetric vibrations of the hydrogens in the methyl groups, respectively.<sup>33,34</sup> In contrast, in the *sps* polarization (Figure 5b), there is only one asymmetric vibrational peak at 2965  $\text{cm}^{-1}$  but no symmetric vibrational signal at 2910  $\text{cm}^{-1}$ , meaning that  $A_{\text{sps},s}$  is zero. According to eq 4, this can happen if  $\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle = 0$  or  $r = 1$ . However, the term,  $\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle$ , exists also in eq 3 and could not be zero unless  $A_{\text{ssp},as}$  is zero, which is not the case, as shown in Table 1. Thus, it leads to the other possibility, i.e.,  $r = 1$ . The value of  $r$  for the methyl groups on Si has never been estimated to our knowledge, and even the value of  $r$  for the methyl groups at the end of alkyl chain has not been agreed upon in the literature, ranging from 1.6 to 4.2.<sup>17</sup> Therefore,  $r = 1$  for the methyl groups on Si may not be too far off from a reasonable estimate. We calculate the average orientation of the methyl

groups in the higher concentration regimes (B, C, and D) with eq 3 under the assumption of a bimodal distribution such that the tilt angle of one methyl group from the surface normal is  $\theta$ , and that of the other is  $110^\circ - \theta$ . If the backbone chain is laid parallel to the interface, the plane of Si and two methyl groups will be almost perpendicular to the interface, and two methyl groups maintain  $110^\circ$  relationship according to the surface normal. Figure 7 shows the average tilt angles of  $\langle \bar{B} \rangle$  and two methyl groups as a function of surface concentration with various values of  $r = 1, 1.6$ , and  $4.2$ . Here,  $\bar{B}$  denotes a vector bisecting the C–Si–C plane. There is no distinctive difference in the tilt angles among the choices of  $r$  value. The average tilt angles are almost constant in regime B, increase marginally in regime C, and decrease slightly in regime D. The overall orientation of the monomeric unit is depicted pictorially in the top corner of Figure 7, where one methyl group is closer to the surface normal and the other is more parallel to the interface.

On the basis of the results presented above, we propose a new set of PDMS chain conformations for different surface concentrations at the A/W, as sketched in Figure 8. In regime A, the PDMS chains are completely disordered and randomly rotating. In regime B, the chains lie on the interface, and both methyl groups point into the air, while one is closer to the surface normal and the other is closer to the interface. In regime C, there are two possible conformations; odd-numbered horizontal folding layers (Figure 8C1), or helices on top of a monolayer (Figure 8C2). If the chains form odd-numbered horizontal folding layers, signals from methyl groups in the first and second layer are canceled out as a result of centrosymmetry, but signals from the outermost (third, fifth, and so on) layer contribute to the VSFS intensity. Moreover, if even-numbered layers were formed, hydrophilic O atoms got in contact with hydrophobic methyl groups or even more hydrophobic air. If the chains form helices on top of a monolayer, signals from the helices would be canceled out because of centrosymmetry, while signals from methyl groups in the first monolayer would contribute to the VSFS intensity.

We should note with some emphasis that this horizontally folding conformation model is totally different from the previously proposed conformation in Figure 3C.<sup>4,35</sup> If PDMS chains in regime C were to undergo a transition from monolayers to helices as they were proposed, the VSF spectral intensity should diminish as a result of an increase in centrosymmetry. Kalachev et al.<sup>30</sup> observed that the surface pressure–area isotherm is reversible, and the surface potential is constant in regimes B and C. Thus, they propose that horizontal folding on top of the monolayer is more probable than helix formation or vertical folding. Our results are consistent with the horizontal folding model. While we are uncertain as to the exact conformations adopted by PDMS in regime D, we speculate that horizontal multilayers of the chain conformation are quite likely. Clearly, we can eliminate the standing helices as shown in Figure 3D since such a standing helix conformation would have diminished the VSFS intensity by virtue of centrosymmetry. Furthermore, the horizontally folding multilayers should have only an odd number of layers for the reasons given above.

It should be noted that the molecular configurations of PDMS at the interface are influenced a lot by the solvent quality of the subphase. The water subphase in this study may be considered as a solvent between good and theta solvents, while toluene is considered as a good solvent.<sup>36</sup>

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### Conclusions

We propose a new set of models for the chain conformation of PDMS monolayers at the A/W. The proposal is based on the experimental deduction of the orientations of the methyl groups from the ratio of the oscillator strengths of symmetric and asymmetric vibrational modes from VSF spectra. We find that the methyl groups are completely disordered at dilute concentrations, while one methyl group points toward the air phase and the other lies almost parallel to the interface at semidilute concentrations. At higher surface concentrations, the PDMS chains form horizontally folding, odd-numbered multilayers instead of standing helices, long advocated in the literature.

Finally, the VSFS technique is found to be a very useful tool for investigating the polymer chain conformation on monolayers as with many systems under the constraints of no centrosymmetry.

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