

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

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Introduction: Polydimethylsiloxane - PDMS

PDMS is the central pillar of siloxane polymers

Its glass transition temperature of $-123\text{ }^{\circ}\text{C}$

Features of PDMS structure:

- low intermolecular force between methyl groups,
- very flexible backbone,
- high Si-O bond energy,
- partial ionic character of the bond

The versatile surface properties of PDMS:

the hydrophilic Si-O backbone along with hydrophobic methyl pendent groups confers surface activity at the air/water interface (A/W)

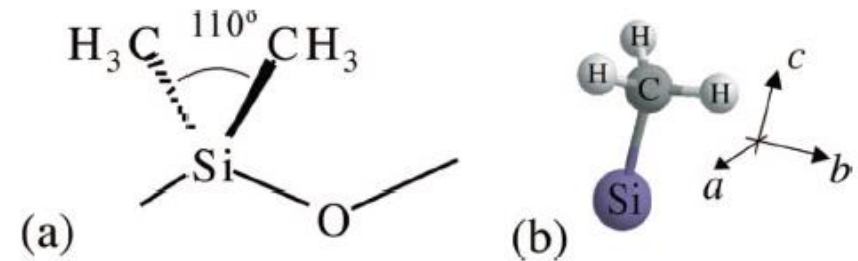


Figure 1. (a) Chemical structure of PDMS and (b) molecular coordinates of the methyl group.

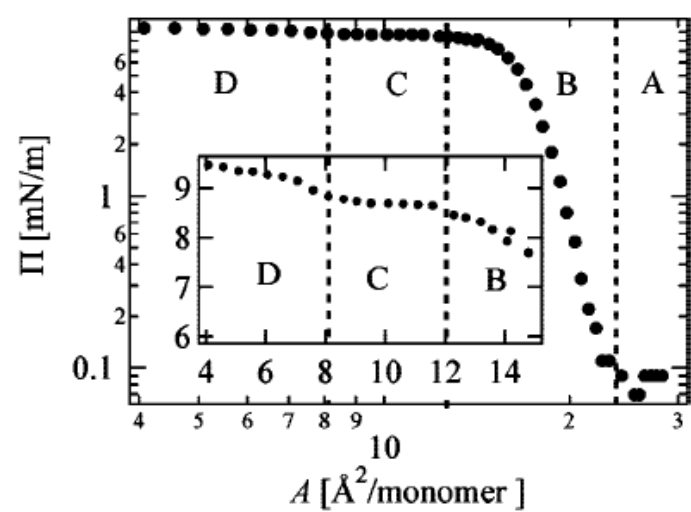


Figure 2. Surface pressure—area isotherm of PDMS monolayer at room temperature. Surface concentrations, the inverse of area/monomer, are purposely demarcated into four regions, A–D, corresponding to distinctive Π – A characteristics.¹⁴

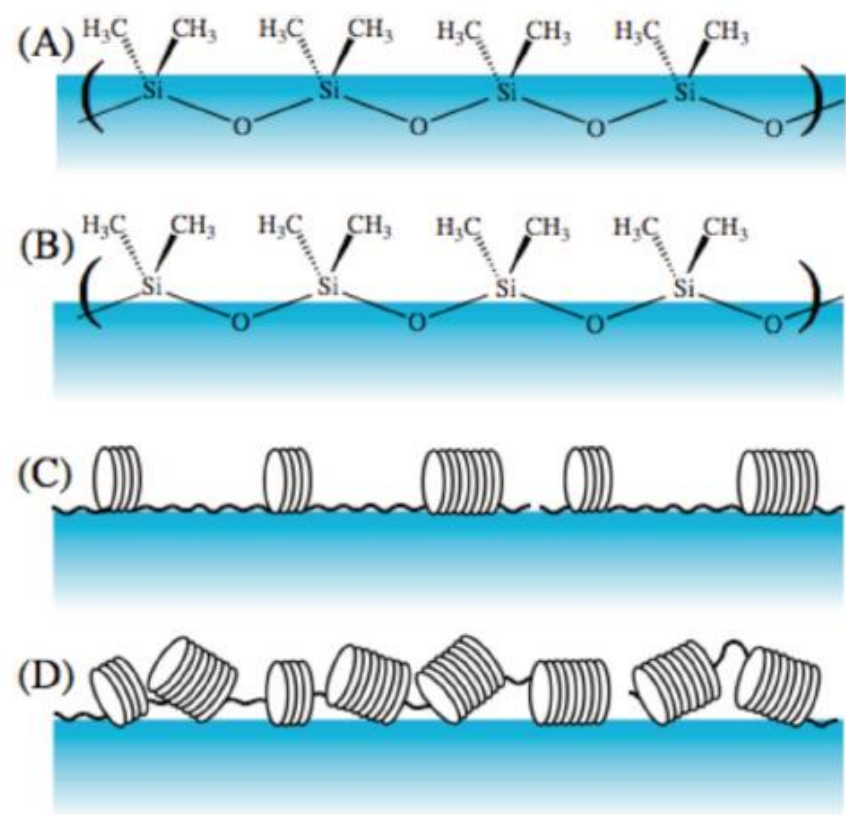
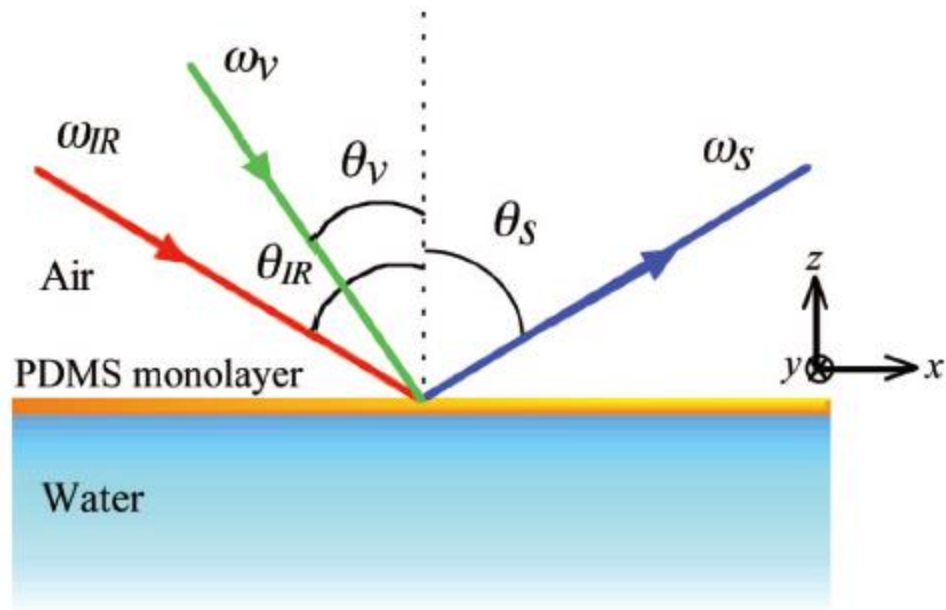


Figure 3. Proposed conformational changes in PDMS isotherms at the A/W. The regions correspond to (A) all Si and O atoms adsorbed onto the interface, (B) some of the Si and O atoms adsorbed (drawn as only O adsorbed for convenience), (C) helices with their axis parallel to the surface, and (D) helices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

VSFS: setup



$$\theta_{IR} = 51^\circ$$

$$\theta_{vis} = 42^\circ$$

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

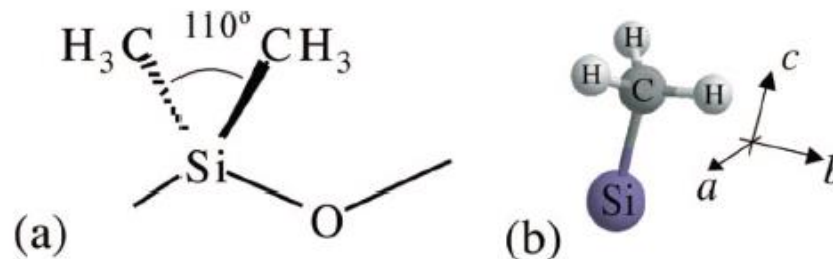


Figure 1. (a) Chemical structure of PDMS and (b) molecular coordinates of the methyl group.

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

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

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

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

$$\langle \cos \theta \rangle \approx \frac{1}{2} (\langle \cos \theta_1 \rangle + \langle \cos \theta_2 \rangle)$$

$$\langle \cos^3 \theta \rangle \approx \frac{1}{2} (\langle \cos^3 \theta_1 \rangle + \langle \cos^3 \theta_2 \rangle)$$

θ_1, θ_2 are the tilt angles of two methyl groups. $\langle \cos^3 \theta_1 \rangle, \langle \cos^3 \theta_2 \rangle$ are obtained by averaging over all possible $\theta_2 - 110^\circ$ from the first tilt angle, θ_1

The average orientations of the two methyl groups:

$$\langle \theta_1 \rangle \approx a \cos(\langle \cos \theta_1 \rangle + \langle \cos \theta_2 \rangle)$$

$$\langle \theta_2 \rangle \approx 110^\circ - \langle \theta_1 \rangle$$

$\langle \theta_1 \rangle, r$ - ???

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

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

^a The subscript “s” is for the CH₃ symmetric vibrational mode, and “as” is for the CH₃ asymmetric vibrational mode. A_n is the oscillator strength of the n th resonant mode, ω_n is the frequency of the n th resonant mode, and Γ_n represents its peak width. The standard deviations of ω_n are less than 1 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^a

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

^a The subscript “as” is for the CH₃ asymmetric vibrational mode.

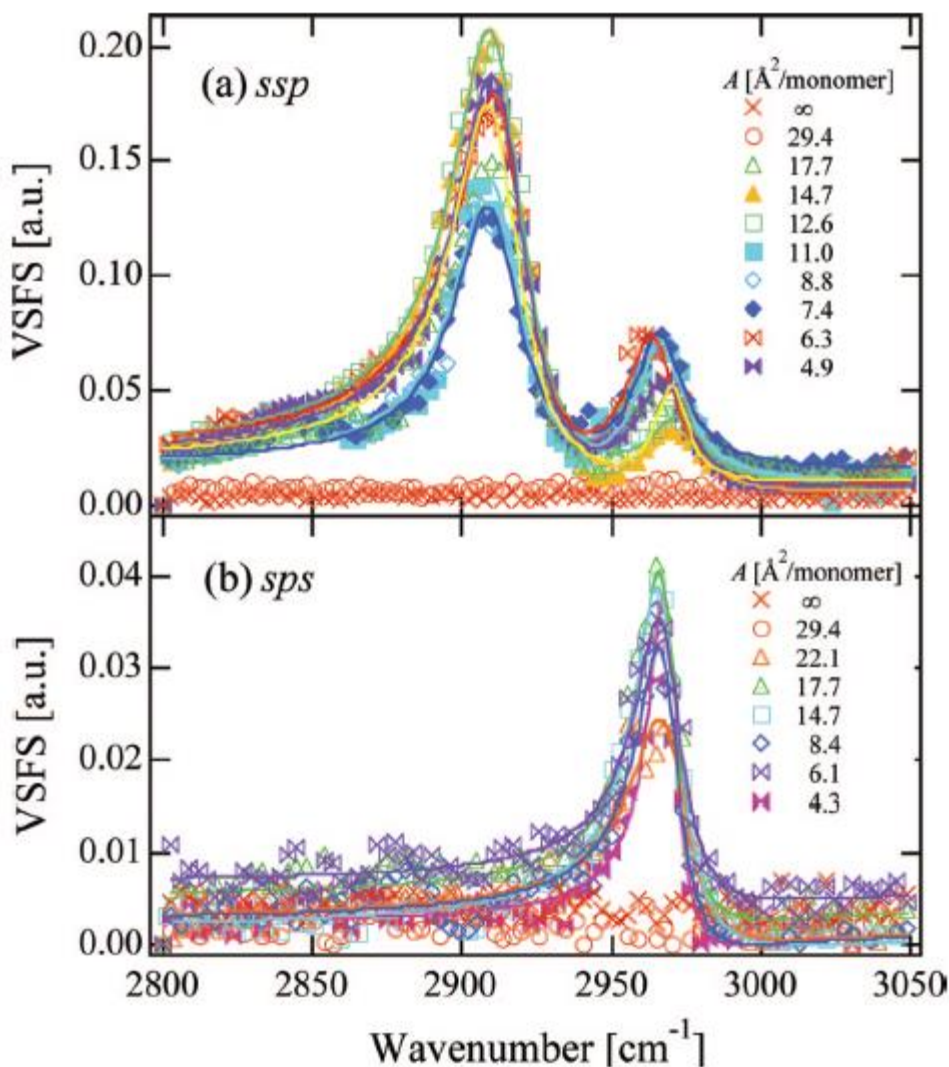


Figure 5. VSFS Spectra of (a) *ssp* and (b) *sps* polarization combinations from PDMS monolayer at the various surface concentrations.

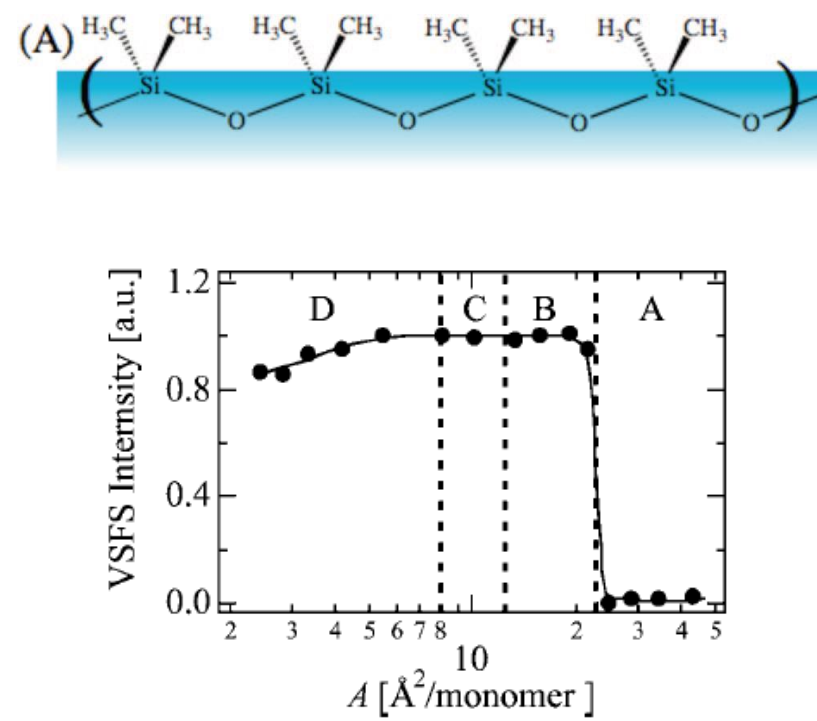


Figure 6. VSFS intensity of *ssp* polarization at 2915 cm⁻¹ as a function of surface area per monomer.

The average tilt angles of $\langle B \rangle$ and two methyl groups as a function of surface concentration with various values of $r = 1, 1.6, \text{ and } 4.2$

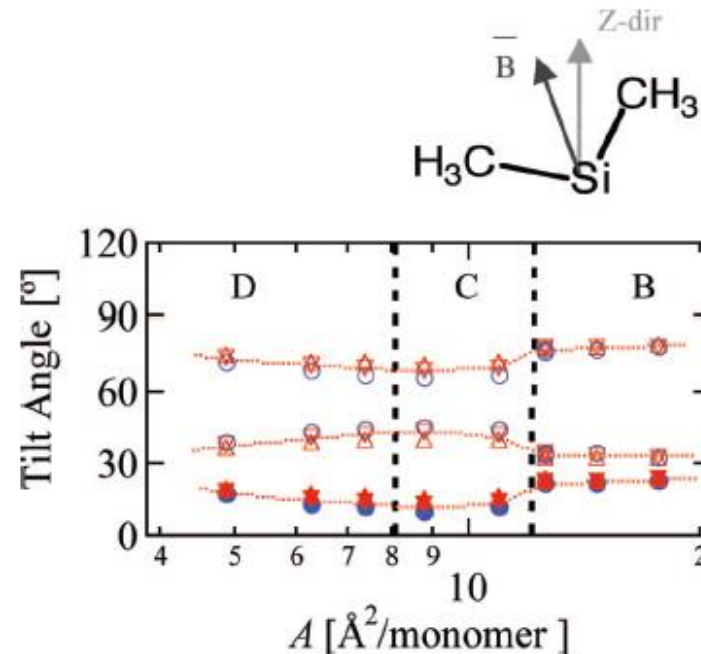


Figure 7. Average orientation of the methyl groups in PDMS on an A/W as a function of surface concentration with three different values of $r = \alpha_{aac}/\alpha_{ccc}$ (circles: $r = 1.0$, lower triangles: $r = 1.6$, and upper triangles: $r = 4.8$). Open symbols are for the each methyl group separated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

A new set of PDMS chain conformations for different surface concentrations at the A/W

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 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.

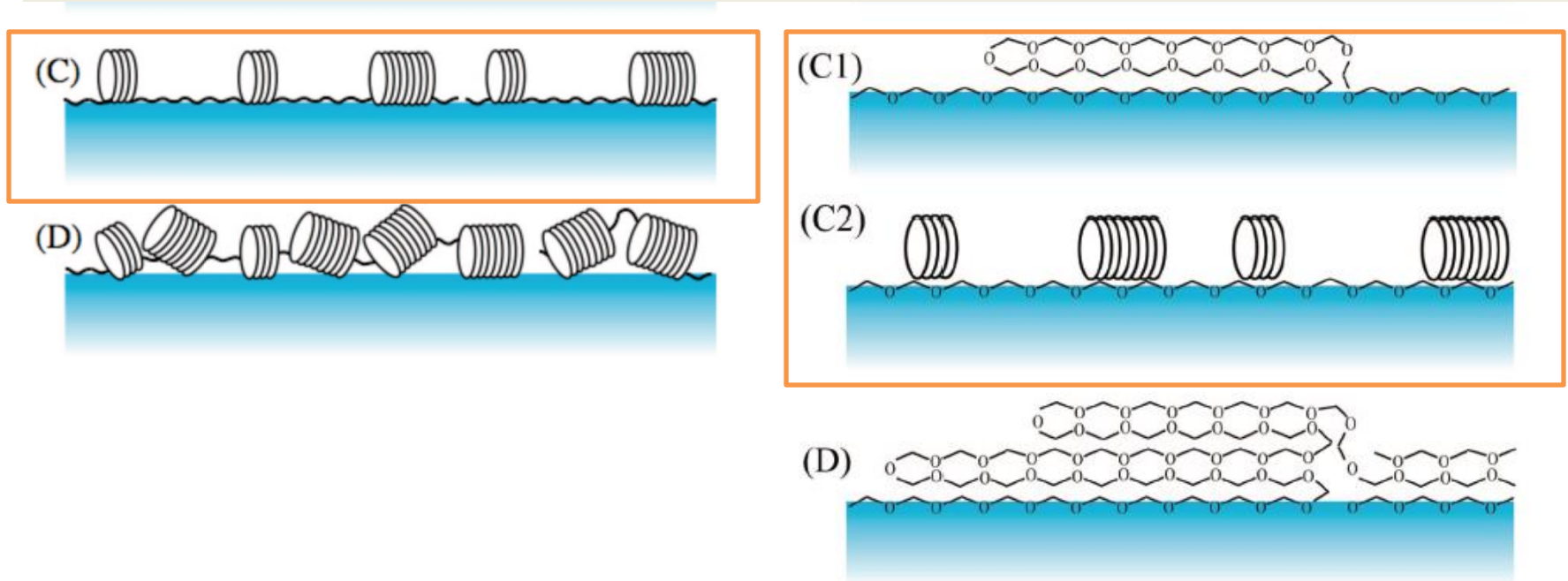


Figure 8. Modified chain conformation model of PDMS isotherms at the A/W. The regions correspond to the same concentration as in Figure 4: (A) randomly rotating chains, (B) monolayers with one methyl group close to the surface normal and the other to the surface, (C) monolayers mixed with horizontal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

Conclusions

- The VSFS technique is useful for investigating the polymer chain conformation on monolayers
- A new set of models for the chain conformation of PDMS monolayers at the A/W
- 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

Materials and Monolayer Preparation

- Deionized water is used as the subphase
- The deionized water with a minimum resistivity of 18 M Ω at the outlet
- The PDMS sample:
 - a number average molecular weight of 10,060 g/mol
 - a polydispersity index of 1.15
- HPLC-grade chloroform 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 is varied from 29.4 to 2.5 Å²/monomer