# Reflection–Absorption Fourier Transform Infrared Spectroscopic Study of Transferred Films of Poly(dimethylsiloxane) Using the Langmuir–Blodgett Technique

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ABSTRACT: Reflection–absorption Fourier transform infrared spectroscopy (RA-FTIR) has been utilized to investigate the tertiary structures of a series of poly(dimethylsiloxane) (PDMS) films transferred to silver substrates using the Langmuir–Blodgett technique. A surface pressure−area isotherm of PDMS of molecular weight of 2400 Da with low polydispersity (PDI of 1.09) was measured on a water subphase at 20 °C. Films were transferred onto silver substrates at various surface pressures associated with regions on the isotherm where structural changes are indicated. The infrared data from the films indicated the structural changes identified by analysis of the isotherm could be related to polymeric backbone orientational adjustments. This was evidenced by relative intensity changes of the asymmetric and symmetric Si−O−Si stretches located at 1050 and 1110 $cm^{-1}$, respectively. Infrared data from the films also showed increases in absorption consistent with varying film thickness. Ratios of the peak intensity of 1265 $cm^{-1}$ for the various films were compared with theoretical and experimentally observed film thicknesses reported by Fox, Taylor, and Zisman.[1] There was a positive correlation between the peak intensity ratios and structural thickness ratios reported by these authors which supports the proposed structures of caterpillar, zigzag, and helical coil. Furthermore, we report new infrared data supporting the model of structural change in the isotherm proposed by Lenk and Koberstein[2] based on the formation of helical coils with varying number of monomeric units per turn which form based on the surface pressure.

## Introduction

Poly(dimethylsiloxane) (PDMS) is one of the most widely used industrial polymers and has found applications in lubricants, mold releases, cosmetics, and antifoaming agents and can also be found extensively in the medical and semiconductor industries.[3] The unique properties that make PDMS so appealing (chemical inertness, insensitivity to temperature extremes, and surface properties) are directly related to its molecular structure.[4] Industrial worth and ease in manipulation therefore make PDMS a useful model system to investigate the implications of molecular architecture on surface properties. For such an investigation to take place, the different configurations of the polymer must first be identified. PDMS is widely known to adopt a series of configurations under compression, including a helical coil (see below). However, what is not well understood is how the configuration of the polymer affects practical surface properties of the material. The Langmuir–Blodgett technique provides an ideal environment for both structural manipulation of the polymer through compression and for the transfer of specific configurations to a substrate for infrared analysis. In order for the polymer to be structurally manipulated and identified, the configurations of the polymer at different points in the surface pressure–area isotherm must first be understood.

Surface pressure–area isotherms of poly(dimethylsiloxane) (PDMS) on water have been investigated for nearly 60 years.[1] The isotherms consist of a number of distinct regions corresponding to the various orientations that the polymeric backbone may adopt. Despite the agreement about the shape of the isotherms, the molecular configurations related to the characteristic transitions are not clear.[1,2,5–9] Lenk and Koberstein provided a thorough summary of the assessments of previous researchers in which conformational changes to the siloxane backbone were interpreted.[2] Their review primarily compared the works of Fox[1] and Noll.[8] From their conclusions the siloxane molecules are believed to exist in three generalized states: caterpillar, zigzag, and coiled helices. Ball model representations of these structures are given by Lenk and Koberstein.[2]

The caterpillar-like structure represents a configuration where all of the silicon atoms are in line in the same plane and all of the pendant methyl groups are pointed away from the water subphase. The backbone is believed to be lying “flat” for this orientation with the oxygen and silicon atoms in contact with the water subphase. The structure exists at low surface pressures. With further compression the polymeric backbone adjusts to the increased surface pressure by adopting a zigzag conformation with every other oxygen (or silicon) associated with the subphase. Further increasing the surface pressure to between 8 and 9 mN/m produces a plateau region in the isotherm in which the helical coil is believed to form.[2] Lenk and Koberstein also identify a small pressure increase identified on the isotherm past the end region for the helical formation which is potentially due to the compression of the helices before chains begin to slide across one another. We refer to as this region as a compressed helical coil region.

Various published studies of the orientations of PDMS are based on other experiments also attempt to elucidate the tertiary structure adopted by the polymer. Soga et al. used infrared dichroism spectroscopy in attenuated total reflection to examine polymer conformations as they evolved over time.[10] Hahn et al. were able to use epifluorescence microscopy and external reflectance infrared (aka reflection–absorption infrared (RAIR or with Fourier transform (RA-FTIR)) spectroscopy to observe monomolecular films spread at the air–water interface on a Langmuir trough.[6] Bae et al. examined how confinement altered the conformations of PDMS by using confocal Raman spectroscopy.[11] Important studies explaining the dipole moments of the backbones were reported by Tsao et al.[12] Examination of the crystalline states of PDMS have also been performed, first by Damaschun[13] by X-ray diffraction and then by Schilling et al. by solid-state NMR.[14] Those results were later evaluated and improved on by an X-ray diffraction study by Albouy which

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showed that the crystalline state of PDMS contains eight monomers per unit cell and that the polymer chains consist of a 4-fold helical configuration.[15]

Although the Hahn study examined the tertiary structures of PDMS films at an air–water interface, no published report has yet examined whether the various configurations of the polymer can be successfully transferred to a substrate, which is crucial to understanding the surface properties of the material in its various structural states.

In this article we will interpret results from a RA-FTIR spectroscopic study directed at investigating the tertiary structure of a series of polymeric monomolecular films transferred by the Langmuir–Blodgett technique onto silver mirror substrates. The purpose of this work is to investigate the structure of the transferred PDMS films from the various regions in the surface pressure—area isotherm with quantitative infrared data. The results will be used in a future study to help understand the relationship between molecular surface structure and practical surface applications. To our knowledge, this is first infrared surface structural investigation of transferred monolayer films of PDMS collected using the Langmuir–Blodgett technique.

## Experimental Section

**Materials.** Poly(dimethylsiloxane) end-capped with trimethylsiloxy and isobutyl groups was purchased from Polymer Source Inc. and was used as received or diluted in reagent grade pentane (98% minimum) purchased from Fischer Scientific. The PDMS used in this study had a molecular weight ($M_w$) of ~2400 (PDMS-2400) and a polydispersity index of 1.09 (as determined by GPC by the manufacturer). PDMS-2400 was also investigated further by MALDI and SIMS mass spectrometry.[16,17] PDMS-2400 was transferred as monolayers or submonolayers onto silver substrates. The silver substrates were silicon wafers coated first with chromium and then by silver by vacuum evaporation. The silicon wafer was purchased from Atomergic Chemetals Corp. The wafer was boron-doped silicon (111) with a 60 mm diameter with a thickness of 350 $\mu$m. The wafer was first cleaned with acetone and then methanol and air-dried. Chromium was vapor-deposited (51 Å) followed by the silver (around 300 Å). The vapor deposition was performed by Dr. Wayne Anderson and Joondong Kim in the Electrical Engineering Department at the University of Buffalo. The chromium layer was necessary to increase the adhesion of the overlayer material. Each mirror was broken into two halves and used as the substrate. The mirrors were cleaned by dipping them in a saturated KOH/isopropanol solution for ~1 min followed by scrubbing and a rinsing with isopropanol and triply distilled water. The mirrors were stored in triply distilled water until their use.

**RA-FTIR.** The data for the RA-FTIR were acquired on a Nicolet Magna FT-IR spectrometer 550 (Nicolet Instruments Corp., Madison, WI). A Harrick versatile reflection attachment with retro-mirror assembly and Harrick double-diamond polarizer (Harrick Scientific Corp., Ossining, NY) was used to collect the reflection–absorption spectra. Each sample was aligned at 78° to the incoming beam for grazing angle reflectance. The sample spectra were an average of 1000 scans. The resolution of the instrument was 2 $cm^{-1}$ with Happ-Genzel apodization. A DTGS detector was used. All of the data were analyzed using the spectral program Grams 386 (Galactic Software, New Hampshire) and by Microsoft Excel.

**Langmuir–Blodgett Trough.** All films were prepared using a KSV model 2200 thermostatted Langmuir trough, with Blodgett style film transfer device (KSV Instrument LTD, Helsinki, Finland). The solutions of polymer were deposited via a 10 $\mu$L Hamilton microsyringe (Reno, NV) onto triply distilled water in the trough. The solution concentrations were ~1.0 mg/mL. The dilute solution was chosen to ensure polymeric chain extension. The initial surface pressure at compression varied from 0.1 to 1.5 mN/m. Isotherms of PDMS are not dependent on the initial surface pressure.[18] The compression rate for each film was 4.0 mm/min and was held at constant surface pressure when a film was being transferred. Films transferred from the caterpillar region were collected at a surface pressure near 0.9 mN/m. Films transferred before the 0.9 mN/m showed no absorbance for the infrared experiment and were discarded. Films transferred at this surface pressure were compared to films transferred at 5.0 nN/m, and differences in intensity and peak ratio were observed corresponding to the formation of two separate structures and therefore were referred to as different structures. Films transferred for helical coil and compact helical coil were collected at 8.5 and 8.9 mN/m. The film was withdrawn from the water/polymer interface at a speed of 2.0 mm/min. Surface pressure measurements were made using a platinum Wilhelmy plate which was flame-cleaned before each experiment. The temperature of the subphase was maintained by circulating temperature controlled water using a model CFT-25 refrigerated recirculator (NESLAB, ThermoScientific, Waltham, MA). To minimize vibrations from the recirculator to the Langmuir–Blodgett trough, the water flow from the cooling system was connected to a mounted adapter by neoprene tubing.

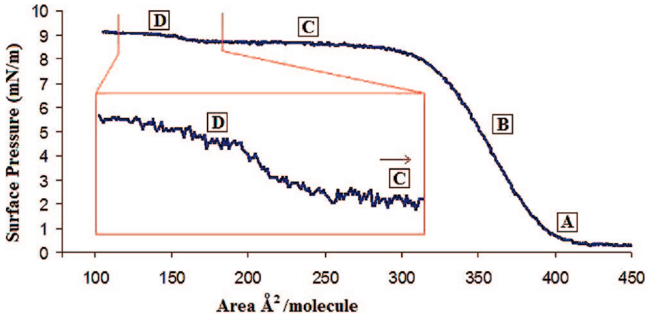

**Figure 1.** Isotherm for PDMS2400 indicating the regions where films were cast using the Langmuir–Blodgett technique.

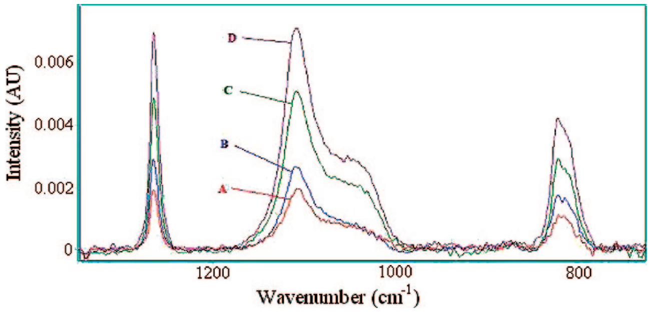

**Figure 2.** RA-FTIRS data for various films collected on silver. Spectral data are identified by letters corresponding to the region in the isotherm where the film was collected.

## Results and Discussion

**Isotherm.** Figure 1 shows a typical isotherm of PDMS-2400 collected on a water subphase temperature controlled at 20 °C. The boxed letters represent the regions where films were collected. Region A, B, C, and D represent caterpillar, zigzag, helical coil, and compressed helical coil films, respectively, as discussed in the Introduction. Following designations derived from Lenk and Koberstein,[2] region A represents the flat polymer backbone chain, region B is a more flexible version of the structure in region A in which the backbone is slightly twisted and bent, and region C represents the coiling of the molecule to form a helix whose axis is parallel to the subphase surface. The small increase observed by position D (see inset in Figure 1) may be due to compression of the helices[2] and will be discussed in more detail later below.

**RA-FTIR Data.** Figure 2 shows representative RA-FTIR data for the systems described in the previous paragraph. The letters identifying the spectral data in Figure 2 represent the regions in the isotherm where those films were collected. Four peaks

**Table 1. Ratios of Peak Intensities from RA-FTIRS Data of PDMS-2400 on Silver Substrates**

| film type | ratio of asym Si−O−Si/ Sym Si−O−Si str | ratio of $Si-CH_3$ bend/ Sym Si−O−Si str | ratio of asym Si−O−Si/ $Si-CH_3$ bend |
|---|---|---|---|
| A | 0.33 ± 0.06 | 1.02 ± 0.06 | 0.33 ± 0.07 |
| B | 0.27 ± 0.07 | 1.08 ± 0.01 | 0.25 ± 0.07 |
| C | 0.418 ± 0.008 | 0.98 ± 0.01 | 0.428 ± 0.008 |
| D | 0.416 ± 0.009 | 0.97 ± 0.02 | 0.431 ± 0.003 |

**Table 2. Ratio of 1265 cm$^{-1}$ Peak Intensity between Films**[a]

| film | divided By A | divided by B | divided by C | divided by D |
|---|---|---|---|---|
| A | | 0.8 ± 0.1 | 0.45 ± 0.06 | 0.36 ± 0.05 |
| B | 1.3 ± 0.2 | | 0.56 ± 0.04 | 0.44 ± 0.03 |
| C | 2.3 ± 0.3 | 1.8 ± 0.1 | | 0.80 ± 0.02 |
| D | 2.8 ± 0.4 | 2.3 ± 0.1 | 1.26 ± 0.03 | |

[a] Film letters correspond to position on isotherm from Figure 1.

in the spectrum were analyzed in detail for this study: the bands at 1265 cm$^{-1}$ ($Si-CH_3$ symmetric bend), 1110 cm$^{-1}$ (Si−O−Si symmetric stretch), 1050 cm$^{-1}$ (Si−O−Si asymmetric stretch), and 815 cm$^{-1}$ ($CH_3$ rocking).[6,10,12]

Three characteristics of the spectra were investigated as potential evidence of structural differences: peak energy positions (wavenumber, cm$^{-1}$), relative peak intensities, and overall spectral intensities. A shift in energy position of a peak when comparing the systems would indicate a change in the chemical environment by either a strengthening or a weakening of the chemical bond energy. It was expected that the helical structure would afford more chemical stability and shift some peak positions to a higher energy or wavenumber, but all peak positions are statistically equivalent for the four systems investigated.

For the investigation of the relative peak intensities, information reported by Tsao and Rabolt regarding the siloxane backbone was used.[12] In their study, they identified the Si−O−Si asymmetric stretch (asym str) and Si−O−Si symmetric stretch (sym str) as a means of interpreting the orientation of the siloxane backbone. The asym str peak is located near 1050 cm$^{-1}$ and is described as having a net dipole moment change parallel to the chain direction of the polymer backbone. The sym str peak is located at 1110 cm$^{-1}$ and has a net dipole change perpendicular to the backbone. To investigate intensity differences for these peaks, relative peak intensities were used to avoid film thickness effects, which will be discussed later in the article. Therefore, in order to determine whether either the asym str or the sym str peaks are changing in intensity between the systems, a ratio of the peak intensities was calculated.

A ratio of the intensity of the asym str and the intensity of the sym str ($I_{1050}/I_{1110}$) for the regions of interest are as follows: D ≈ C > A ≈ B (see Table 1). In addition, the peak ratio of 1265 cm$^{-1}$ to 1110 cm$^{-1}$ ($I_{1265}/I_{1110}$) shows statistically equivalent values while the ratio of $I_{1050}/I_{1265}$ shows higher ratio values in the spectra for C and D films when compared to that from the A and B spectra. The $I_{1050}/I_{1110}$ ratio suggests either a decrease in the intensity of the symmetric Si−O−Si stretch or an increase in the intensity of the Si−O−Si asymmetric stretch in the polymer backbone for the C and D films when compared to the A and B films. Either an increase in the $I_{1050}$ or a decrease in $I_{1110}$ supports the idea that the polymer is adopting an orientation that has a higher degree of orthogonality with respect to the substrate surface. Assuming that films pulled from region A are composed of PDMS chains adsorbed in a linear orientation with the backbone lying "flat" on the substrate the increase in the asym/sym ratio suggests some deviation away from this flattened orientation, indicating that the backbone chain is lifting. This is in agreement with the polymer adopting a flat helical coil structure. A comparison between caterpillar and zigzag from the $I_{1050}/I_{1265}$ ratio was not clear; the differences in the values of the ratios were not statistically significant. The structures should be very similar.

A comparison of the overall spectral intensity was made by calculating all possible ratios of the peak intensities *between* the spectra of different types of films. For example, Table 2 shows the ratio of the 1265 cm$^{-1}$ peak between the multiple systems. Column one identifies the film type while row one explains the film intensity that was divided into the film intensity from column one. For column two the spectral data show that the ratio of the peak intensity of 1265 cm$^{-1}$ for film B divided by the peak intensity of 1265 cm$^{-1}$ for film A ($B_{1265}/A_{1265}$) has a ratio value of 1.3 ± 0.2. From the same column, $C_{1265}/A_{1265}$ has a value of 2.3 ± 0.3 and $D_{1265}/A_{1265}$ has a value of 2.8 ± 0.4. Other ratios between the films (e.g., $C_{1110}/A_{1110}$) produce similar ratio values. The consistency of peak intensity change between the films is interpreted as being due to increasing film thickness or monomer areal density. The data suggests an increase in film thickness or monomer areal density such that A < B < C < D. Since the Langmuir–Blodgett method of film casting intrinsically forms monomolecular systems, it is assumed that change in thickness for the films is due to the tertiary structure of the polymeric backbone and is not due to the formation of a multilayer system.

Table 3 displays the ratio values for the reported thicknesses of the various types of PDMS films that form according to Fox and Zisman.[1] The values for the thicknesses found in columns two and three of Table 3 were determined by Fox and Zisman by using both the Fischer−Hirschfelder atom models approach (ball model) and through experimental observations (observed). They were able to construct ball model systems of the polymer conformations for caterpillar, zigzag, and a six-monomer helical coil. Fox and Zisman determined that the helix may contain either six or seven monomers per turn based on the temperature of the subphase. Experimentally, they observed that a six-monomer helix would have a thickness of 12.5 Å while a seven-monomer helix would have a thickness of 14 Å. The ball model could not be manipulated into a diameter for a coil with more than six monomers per turn so values for the ball model for compact helices are omitted. In addition, Albouy determined from X-ray diffraction that PDMS has eight monomers per turn.[15] A value of eight monomers per turn was not calculated or observed by Fox and Zisman, so a rough estimate based on the diameters of the six- and seven-monomer coils was used to calculate a thickness of 15.5 Å. It should be noted that the information from the Fox and Zisman study used values for the observed thicknesses that were calculated from a film of a PDMS heptadecamer (17 repeat units). They pointed out, however, that only a very low molecular weight polymer that contained eight or less repeat units would deviate from these calculations. Granick also determined in an independent study that the surface pressure in the transition region is independent of molecular weight.[7] We can therefore assume that the observed thickness measurements and the values for the compact helices are suitable for a comparison to our films.

For the comparison of monolayer thicknesses, the peak at 1265 cm$^{-1}$ from the infrared data was utilized on the basis of its sharp peak formation, ease of assigning intensity, and narrow width. Again, since all peaks investigated change in approximately the same ratio, it can be inferred that the change in intensity is due to film thicknesses. A comparison was then made on the basis of ratios for the structures. For example, the ratio of the thickness for a caterpillar structure divided by the thickness for the zigzag structure for both observed ($OBS_{cat}/OBS_{zig}$) and ball model approximations ($BM_{cat}/BM_{zig}$) were compared with the ratio of an A film intensity at 1265 cm$^{-1}$ relative to the B film's intensity at the same peak position ($A\ I_{1265}/B\ I_{1265}$) and plotted. The first evaluation compared the ratios

**Table 3. Ratio of Reported Thicknesses of for the Siloxane Molecule**[a]

| film | ball model film thickness (Å) | Fox/Zism an observed thickness (Å) | ball model ratio caterpillar | observed ratio caterpillar | ball model ratio zigzag | observed ratio zigzag | ball model helix | observed ratio helix | ball model ratio compact (7) | ball model ratio compact (8) |
|---|---|---|---|---|---|---|---|---|---|---|
| caterpillar | 5.6 | 5.9 | | | 0.71 | 0.75 | 0.45 | 0.46 | 0.40 | 0.36 |
| zigzag | 7.9 | 7.9 | 1.4 | 1.3 | | | 0.63 | 0.62 | 0.56 | 0.51 |
| helix-6 monomer | 12.5 | 12.7 | 2.2 | 2.2 | 1.6 | 1.6 | | | 0.89 | 0.81 |
| compact helix-7 monomer | | 14 | | 2.4 | | 1.8 | | 1.1 | | |
| compact helix-8 monomer | | 15.5 | | 2.6 | | 2.0 | | 1.2 | | |

[a] The ball model method is based on Fischer−Hirschfelder atom models, and the observed thickness were reported by Fox and Zisman.

of the calculated ball model thicknesses to the spectral intensities of A $I_{1265}$, B $I_{1265}$, and C $I_{1265}$. The second evaluation compared ratios calculated using data for the observed thicknesses of caterpillar, zigzag, and a six-monomer helix ($OBS_{cat}$, $OBS_{zig}$, $OBS_{6hel}$) to A $I_{1265}$, B $I_{1265}$, and C $I_{1265}$. Linear regression plots (not shown) were utilized to show the agreement between ratios. The linear regression using the ball model approximation was 0.98 while the comparison of the observed experimental thicknesses yielded a linear regression of 0.99. The positive correlation between the data sets supports the idea that the LB films collected from the various points on the isotherm contain similar structural ratios to those presented from theoretical calculations and experimental observations and that the films were transferred properly.

For the validation of the compact helices, another evaluation was made using the experimental thickness data and also the values for the seven-monomer and eight-monomer compact helix compared to D film spectral data. For the first comparison the experimental data for caterpillar, zigzag, six-monomer helix, and the thickness for the seven- or eight-monomer helix were compared to the spectral data of A, B, C, and D films. The linear regression for the seven-monomer compact helix and the eight-monomer compact helix was 0.97 and 0.98, respectively. The values were expected to be similar due to the already high linear regression for the other structures considered. Another plot was made using only the ratios of the six-monomer helix and the seven/eight-monomer helix. The purpose of this plot is to determine which of the two compact helical coil models (seven or eight monomers per turn) is more relevant to the data observed by Fox and Zisman. The linear regression for the seven-monomer helix is 0.94 and is 0.99 for the eight-monomer helical model. The linear regression plots support the formation of a compact helical coil, specifically the formation of a helix with eight monomers per turn. This is in agreement with Albouy's X-ray diffraction study of crystalline PDMS.[15]

## Conclusions

The conformations of PDMS were examined as transferred monomolecular films on mirrored substrates using reflection–absorption Fourier transform infrared spectroscopy. The results from spectral intensity ratios suggest different orientations of the siloxane backbone for films collected at different surface pressures. Specifically, the molecular tertiary structures of caterpillar, zigzag, and a six-monomer helix were examined. A film thickness comparison was made using both theoretical and experimentally reported results and strongly suggests the proper transfer of those structures onto the substrate. Additionally, evidence is provided which supports the formation of a compact helical coil consisting of eight monomers per turn. This structure is believed to exist where a slight surface pressure increase is noticed after the plateau region in the polymer's isotherm. The information gathered here will be of use to future studies of transferred Langmuir–Blodgett films, specifically to secondary ion mass spectrometry (SIMS) investigations of model tertiary systems.

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