

Chemical Imaging in a Surface Forces Apparatus: Confocal Raman Spectroscopy of Confined Poly(dimethylsiloxane)

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Confocal Raman spectroscopy has been implemented within the molecularly thin films of a surface forces apparatus. Applying this technique to an initial system, we investigate the confinement and shear-induced changes in the Raman spectra of poly(dimethylsiloxane) (PDMS) liquids confined between atomically smooth mica surfaces at thicknesses less than the unperturbed radius of gyration of the polymer. We focus on stretch vibrations of the PDMS methyl group, whose net orientation is perpendicular to the chain backbone. When PDMS was confined to a thickness of approximately the unperturbed radius of gyration (3.5 nm) but no shear, the Raman intensity of the methyl group was anisotropic in the x - y plane, signifying that chains oriented preferentially parallel to the confining surfaces. Relative to the bulk fluid, the relative intensity of the asymmetric to symmetric carbon-hydrogen stretch (2965 and 2907 cm^{-1} , respectively) was enhanced, indicating that asymmetric vibration was enhanced by confinement. Measurements using polarized radiation showed coherent planar anisotropy in the x - y plane whose direction varied stochastically from experiment to experiment. It seems that although coherent in-plane alignment was favored, no preferential alignment direction was favored in the absence of shear. Application of shear caused the time-averaged polymer conformations to become more nearly isotropic in the plane of shear. These measurements are considered to represent the first chemical imaging of chemical species within the contact area of a surface forces apparatus.

Introduction

The structure and dynamics of molecular constituents in soft condensed matter have been observed to change fundamentally when the system becomes geometrically confined.^{1,2} Physical properties that change with confinement include the effective viscosity, the diffusion constant, the melting point, and the structure. Here we are concerned with confinement between single crystals of mica in a surface forces apparatus (SFA). Customarily the SFA technique is used to measure the interaction forces between two surfaces as a function of separation from the deflection of a leaf spring supporting one of the surfaces; the separation, down to film thicknesses of nanometers or even less, is measured by multiple beam interferometry. Modification of the instrument allows measurements of both lateral (frictional) and normal (attractive or repulsive) forces between two surfaces that are in relative motion. Due to its capacity for constraining the intersurface separation at close distances while measuring shear forces, the SFA (and its cousin, the atomic force microscope) have now become essential tools in colloid and surface science.

Force measurement carries no direct information, however, regarding molecular composition, structure, conformation, or mobility. With this in mind, this laboratory has been working to integrate the SFA with spectroscopic probes. Previously we reported a fluorescence-based method³ and ensuing studies using that method^{4,5} to investigate the translational diffusion of dye molecules

embedded at nanomolar concentration within confined liquids. But although single-molecule sensitivity is attractive, this approach presents the drawback that the fluorescent probe molecule might itself potentially modify the structure and dynamics of the matrix within which it is embedded. Furthermore, direct information about molecular conformations is not afforded by this fluorescence method.

For these reasons, it is also desirable to develop methods to reflect molecular conformations directly. In a previous work, the photoemission of confined conjugated polymers was reported.⁶ Here we present our first experiments using vibrational spectroscopy. Infrared spectroscopy was considered as a technique, but its implementation was deferred at the present time for several reasons: first, because of the difficulty of separating the sample signal from the background, that is, of separating the molecularly thin sample absorption of interest from background absorption by the instrumental apparatus through which an infrared beam must pass on its way to a sample, and second, because of the interference fringes produced when a broadband infrared beam is directed at parallel plates. A confocal geometry circumvents both problems.

Here we describe findings using confocal Raman spectroscopy to study how confinement alters the conformations of the polymer liquid, poly(dimethylsiloxane) (PDMS). Advantages of Raman studies include (1) dye-free measurement, (2) direct experimental observables at the molecular level, (3) orientational information using polarized light, and (4) chemical information from peak position and bandwidth analysis.

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Experimental Section

A detailed account of the experimental setup will be presented elsewhere. Briefly, the main experimental requirement enabling Raman measurement in a SFA was to create an optical window through which the Raman measurements could be made in one region of the visible spectrum, while at the same time performing interferometry measurements, to measure surface–surface spacing. The silver sheets normally used for interferometric measurement of surface spacing⁷ were replaced by multilayer dielectric coatings. Electron-beam deposition was used to coat 13 alternating layers of TiO_x and Al_2O_3 with high reflectivity in the region 700–800 nm and transparent below 700 nm, thus, enabling not only the determination of film thickness by interferometry but also transmission of incident laser light and the resulting Raman scattering. Similar multilayer dielectric coatings, developed for application to fluorescence measurements, are described in more detail elsewhere.²

As the excitation source, an Ar^+ laser (Melles-Griots, 543-BS-AO3) was used at 488 nm. The average power at the sample stage was kept <20 mW. Laser beam polarization was controlled at the first level using a half-wave plate and then refined using a Glan-Taylor polarizer, which resulted in a contrast ratio of $>10^5$. The laser beam size was expanded five times by a Galilean beam expander to overfill an aspheric lens to obtain a diffraction-limited beam size.

A second experimental innovation in these experiments is that the laser beam was focused by an aspheric lens with numerical aperture (N.A.) = 0.68 and working distance of 3 mm. Customarily, an objective lens is considered to be preferable to an aspheric lens because it yields a better optical image with better correction for aberrations, but in the present application this presented no great advantage because we focused a monochromatic laser beam and collected the Raman signals from a spot source. An aspheric lens presented the advantage, in the present application, that it possesses longer working distance for the same numerical aperture. This was important because the sample was buried between two cylindrical lenses, each of them ≈ 2 -mm thick. Additional advantages of an aspheric lens included its compact size, higher throughput due to a singlet lens, and inexpensive cost. As implemented here, the height of the confocal excitation spot was $11 \mu\text{m}$ and the diameter was $\approx 0.3 \mu\text{m}$.

The scattered Raman signal was collected by the same aspheric lens and focused to a $100\text{-}\mu\text{m}$ pinhole by a tube lens to reject out-of-focus signals including fluorescence background from mica sheets and supporting lenses. After filtering laser scattering using a holographic notch filter, the scattered Raman signal was dispersed by a 0.5-m spectrometer and detected by a liquid nitrogen cooled CCD (Roper Scientific LN/CCD-1340/400-EB/1).

PDMS purchased from Polymer Source was used without further purification. As characterized by the manufacturer, the number-average molecular weight was 7060 and the ratio of weight-average to number-average molecular weights was 1.07. Droplets of the PDMS were placed between freshly cleaved mica sheets, within a SFA modified to allow these confocal measurements.

Results

Figure 1 shows a typical Raman spectrum of the PDMS bulk liquid; this spectrum was obtained when the mica surfaces were separated by many micrometers and is typical of Raman spectra obtained previously by many others.⁷ Intense stretching vibrations of the methyl group appear at 2965 and 2907 cm^{-1} , methyl bending vibrations appear at 1412 and 1262 cm^{-1} , Si– CH_3 rocking vibrations appear at 862, 787, and 687 cm^{-1} , and Si–O–Si stretching vibrations appear at 488 cm^{-1} . The inset in Figure 1 shows the molecular structure of the PDMS repeat unit.

Vibrations along the backbone of the PDMS chain (the Si–O vibration) afford in principle the most direct measure of how the polymer chain orients, but unfortunately the intensity of this Raman signal was too weak to be detected

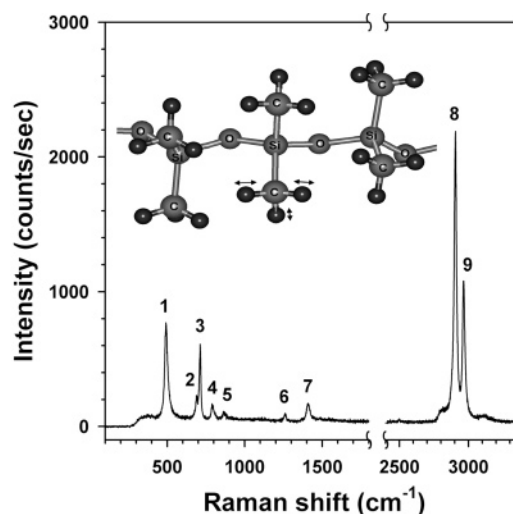


Figure 1. Raman spectrum of PDMS obtained in the apparatus described here. The numbers next to the vibrational peaks represent (1) Si–O–Si symmetric stretching (488 cm^{-1}), (2) Si– CH_3 symmetric rocking (687 cm^{-1}), (3) Si–C symmetric stretching (708 cm^{-1}), (4) CH_3 asymmetric rocking + Si–C asymmetric stretching (787 cm^{-1}), (5) CH_3 symmetric rocking (862 cm^{-1}), (6) CH_3 symmetric bending (1262 cm^{-1}), (7) CH_3 asymmetric bending (1412 cm^{-1}), (8) CH_3 symmetric stretching (2907 cm^{-1}), and (9) CH_3 asymmetric stretching (2965 cm^{-1}). The inset shows the molecular structure of the PDMS repeat unit and also the atomic motion of the stretch vibration of the methyl group, whose quantification is pursued in the succeeding figures.

in thin films. To investigate the effect of confinement on polymer conformations, the intense stretch vibrations of the methyl group located at 2900 cm^{-1} were monitored instead. The molecular structure depicted in Figure 1 illustrates that the stretching vibrations of the methyl group are nearly perpendicular to the polymer backbone.

Within a SFA equipped for shear,⁸ the PDMS liquid was confined to the thickness of 3.5 nm, which we estimate to be comparable to the thickness of a random coil. With the application of pressure (Hertzian pressure ≈ 3 MPa, that is, force/area ≈ 2 MPa), the PDMS resisted being squeezed out. When a glue was used to mount the mica, the glue was comprised of *sym*-diphenylcarbazide (Figure 2). In other experiments (Figures 3 and 4), glue was applied at four edges of the lens and we did our best to eliminate the air gap trapped in the center. Both methods resulted in a flattened area at the apex of the crossed cylinders over which the mica was draped, the pressure causing the cylindrical mica sheets to deform. By taking confocal Raman spectra at many positions, a contour map of the contact area was obtained. The peak intensity of the methyl group vibration was recorded for 1 min at spots spaced by $10 \mu\text{m}$ inside the contact area, and at spots spaced by $50 \mu\text{m}$ outside the contact area. In Figure 2, one sees that the intensity of the Raman signal was higher the thicker the film. Detailed analysis of contour plots of the Raman intensity, which were taken at the frequency 2907 cm^{-1} (CH_3 symmetric stretch), shows that the point of flattened contact was circular in shape with a diameter of $200 \mu\text{m}$. This diameter agrees with the optical interferometric measurements that we performed in parallel. The image in Figure 2 is considered to represent the first chemical imaging of the contact area in a surface forces experiment. Whereas traditional multiple beam interferometry produces a spatial image of spacing between

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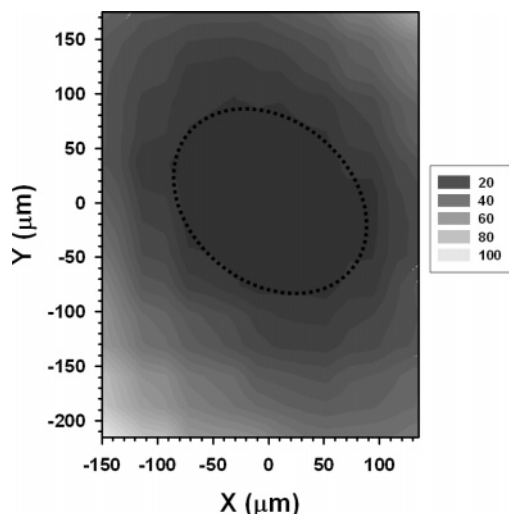


Figure 2. Contour map in the x - y plane of the intensity of the methyl stretch vibration (2907 cm^{-1}) recorded after confining the PDMS to a thickness of 3.5 nm such that the mica sheets flattened at their apex to form parallel plates. The contact spot of minimal thickness is slightly elliptical. The legend shows relative intensity (arbitrary units) denoted by different levels of grayscale.

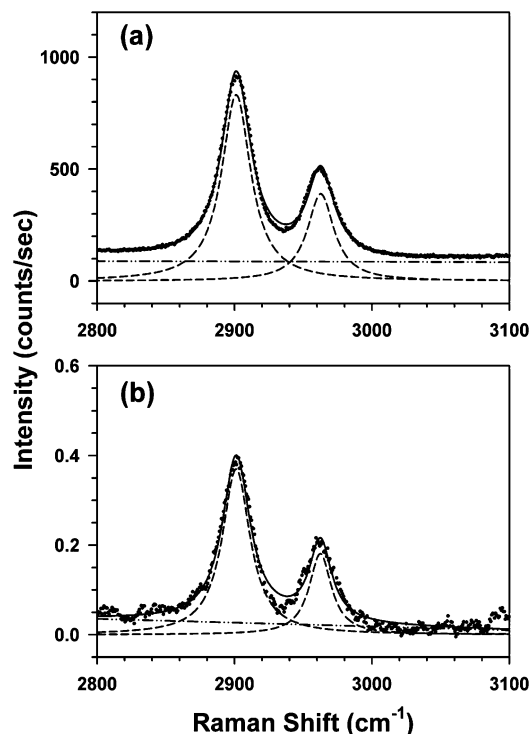


Figure 3. Raman spectrum of PDMS in the region of methyl stretch (symmetric and asymmetric carbon-hydrogen stretch at 2907 and 2965 cm^{-1} , respectively) is compared for the bulk fluid (panel a) and a film 3.5-nm thick (panel b). Curve-fitting used to obtain data in Figure 4 is indicated by dotted lines. The ordinate scale in panel a is arbitrary, but the intensity relative to that in panel b is quantitative. In panel b, the noise level is ≈ 0.04 counts/s, meaning that the signal-to-noise of the symmetric methyl stretch vibration at 2907 cm^{-1} , analyzed in Figure 4, was a factor of ≈ 10 .

the mica surfaces,⁹ the measurements in Figure 2 show instead the quantity of chemical species within the contact area. This approach can also be applied to map out the spatial distribution of different chemical species within

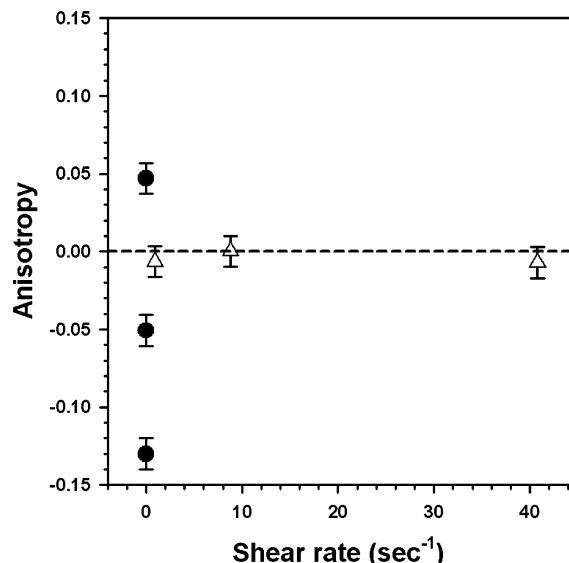


Figure 4. Raman anisotropy of the symmetric methyl stretch vibration, defined as $A = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$, where I_{\parallel} and I_{\perp} represent the peak intensity parallel and perpendicular to the potential shear direction, respectively, is plotted against the peak shear rate for films 3.5-nm thick. The peak shear rate was varied by controlling the shear amplitude during sinusoidal excitation at 1.4 Hz. Circles denote data taken at rest; triangles denote data taken during shear. The dashed line shows zero anisotropy, characteristic of the bulk fluid at rest.

a confined mixture. The method to do so is based on determining the relative intensity of Raman peaks from the mixture components and how this depends on spatial position, but no examples of this are presented at this time.

We turn now to more detailed analysis. Typical spectra in the region of carbon-hydrogen vibrations are shown in Figure 3, for the bulk liquid (panel a) as well as for a film 3.5-nm thick (panel b). The peak vibration frequencies of the methyl groups under confinement are the same as in the bulk fluid, within experimental uncertainty. To observe that the chemical environment of methyl group vibration is essentially unaltered by confinement means that the interaction between these polymer liquids and mica surfaces is not strong enough to affect the vibrational frequencies of methyl group vibrations; it also signifies that the interaction energy between the methyl groups is nearly the same as in bulk liquids.

On the other hand, one notable difference between these spectra is a change in the relative intensity of the asymmetric and symmetric stretch (2965 and 2907 cm^{-1} , respectively). Under confinement this intensity ratio increased to 0.57 from 0.50 in the bulk, indicating that the asymmetric character of vibration was enhanced under confinement. Although molecular vibrations are localized, they depend on conformations of the molecule, which appeared under confinement to become anisotropic relative to the bulk state.^{10,11}

A few experiments were performed in which polarized Raman signals were detected. To enable these measurements, care was needed owing to the birefringence of mica. We carefully mounted the mica sheets to align one of the optical axes of mica parallel to the potential shear direction, and the polarization of the laser beam was aligned parallel or perpendicular to this axis to minimize

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polarization changes induced by birefringence of the mica sheets. For quantification, the Raman anisotropy (A) was defined as $A = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$, where I_{\parallel} and I_{\perp} represent the peak intensities of the symmetric methyl stretch vibration parallel and perpendicular to the potential shear direction, respectively.

In Figure 4, the anisotropy obtained in these preliminary measurements is presented. The numbers are small, but it is striking that the anisotropy was finite; this indicates the existence of net lateral orientation over the diameter of the confocal spot. Also striking is that the magnitude and even the sign of anisotropy varied from experiment to experiment. It is hard to quantify the amount of lateral ordering based on only two polarization measurements of vibrations of methyl side groups. However, it is remarkable that two different measurements gave not only different numbers but also different signs. This suggests that the orientation of conformational anisotropy was random. It may imply that the interaction between polymer and mica surfaces was too weak to induce a preferential surface-mediated lateral ordering yet that the act of squeezing the PDMS to a small thickness itself generated preferential ordering but without a preferred direction. The measurements in Figure 4 refer to a single experiment, and the error bars denote uncertainty of the fit. However, the generality of the conclusion was confirmed: first, qualitatively in independent experiments using newly mounted mica sheets, and next, from other experiments with a PDMS sample of higher molecular weight, as will be reported elsewhere. However, not yet known is the extent to which anisotropy differed from spot to spot within the same contact area.

To investigate the influence of shear perturbation on these polymer conformations, we applied an oscillatory shear perturbation at 1.4 Hz using piezoelectric methods described previously.⁸ The peak velocity during shear, the product of shear amplitude and radian frequency, was normalized by the film thickness to give the peak shear rate. In Figure 4, the Raman anisotropy of the methyl group (A) is plotted as a function of the peak shear rate. It is striking to observe that the effect of shear was to make the polymer conformation more isotropic. Ongoing Raman experiments involving the confined liquid crystal 5-cyanobiphenyl, confirm this conclusion. Mechanical

experiments of confined PDMS led to the opposite conclusion, however.¹² The extent to which this difference should be attributed to the fact that PDMS of higher molecular weight was studied in the mechanical experiments¹² or to the fact that our anisotropy measurements in these initial experiments were time-averaged over the period of oscillation is not yet clear. Possibly the relatively low shear rates investigated until the present did not present a shear perturbation strong enough to induce conformational ordering yet were strong enough to disrupt the anisotropy produced when the films were squeezed to the confined thickness.

Looking to the future, this study shows the feasibility of quantitative Raman spectroscopy experiments within a SFA. The experiments yield spatially resolved information regarding not only the chemical makeup of the confined film but also how molecular conformations differ between a bulk fluid and confined films. Although the technique is at present limited to the study of confined molecules whose Raman scattering is intense, future technical improvements may enhance the sensitivity to the point that a wider range of fluids can be investigated and also to the point that the line width analysis will reveal how confinement and shear alter the process by which vibrational energy decays.¹³ It is hoped that when applied to other systems, Raman experiments will clarify the controversial issue of the conditions under which alkanes order under confinement.¹⁴ Taking a broader view, the significance is to point the way toward new methods to obtain a direct molecular understanding of how molecules structure in thin films, as well as how energy is lost in the process known as friction.

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