Infrared Dichroism and Surface Conformational Dynamics of Adsorbed Poly(dimethylsiloxane)

Iwao Soga[†] and Steve Granick[*]

Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801

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ABSTRACT: We examined polymer conformations at a strongly adsorbing solid surface and their evolution with elapsed time during the adsorption process. Poly(dimethylsiloxane) (PDMS: $M_w = 118\,000$; $M_w/M_n = 1.16$) was allowed to adsorb onto oxidized germanium from dilute carbon tetrachloride solutions. The mean backbone orientation was found to change even after the mass adsorbed had saturated; its conformation was determined using infrared dichroism spectroscopy in attenuated total reflection (FTIR−ATR). The dichroic ratio (D) of the Si−O−Si and Si−CH$_3$ stretch vibrations showed the PDMS backbone to be preferentially horizontal to the surface ($D \cong 0.9$ at early adsorption times) and to grow increasingly flattened with increasing adsorption time. However, as the adsorbed amount increased with higher solution concentrations, the average orientation was less flattened. Chain flattening during the adsorption process was also slower, the higher the adsorbed amount, reflecting molecular crowding within more densely occupied layers. During desorption into the pure solvent, the evolution of the dichroic ratio could be described by the hypothesis of a bimodal configurational distribution.

Introduction

The process of polymer adsorption, from a random coil in a solution to an equilibrium adsorbed polymer, is not simple. At the initial stage of this process the adsorbed polymer shape reflects the conformation with which it touches to the surface. Then it proceeds toward a more equilibrated state described by thermal statistics. Properties of the equilibrated state have been much studied by both theoretical and experimental techniques,[1−3] but attainment of the equilibrated state sometimes takes a long time because polymer chain mobility is so restricted by attachment to the surface as well as by entanglement with neighboring chains.[4,5] It is interesting to study this intermediate state in its own right: the time period during which the adsorbed polymer is in the process of relaxing toward conformations of lower energy.

Some recent studies have focused on this transition state, and several types of experiments and simulations have been done.[6−10] Hydrodynamic thickness studies show that rearrangement occurs inside the adsorbed layer.[6] Displacement experiments of polystyrene on oxidized silicon also show rearrangement of adsorbed polymer, such that the polymer adsorbs more tightly with increasing adsorption time.[7] On the other hand, bound fraction and infrared dichroism experiments concerning a more strongly adsorbing system, poly-(methyl methacrylate) on oxidized silicon, reveal large conformational differences between first-adsorbed polymers and later-arrived ones, without perceptible subsequent changes over times as long as many hours.[8] These results emphasize that the adsorbed polymer conformation can be varied by the history of the adsorption process and show that in some cases the surface composition becomes trapped in metastable states. When one considers that responses over long time scales are characteristic of numerous other polymer phenomena, to find the prominence of relaxation processes within adsorbed layers is perhaps natural.

In this study, polymer conformations in the adsorbed state were probed from the polymer backbone orientation measured by infrared dichroism. The average direction of the polymer backbone was measured from the infrared (IR) dichroism of a polymer, poly(dimethylsiloxane) (PDMS), whose backbone carries an infrared-active vibration. Static states of PDMS adsorption have been studied by others previously using various techniques.[11−14] In employing IR dichroism in the present study, we exploit the fact that the Si−O−Si sequence along the backbone shows stretch vibrations with strong IR absorbance. The pendant Si−CH$_3$ groups also display strong IR absorbance and also reflect the backbone orientation to the extent that the mean angle to the backbone is known. The dipole moments of these two bands are parallel to and roughly perpendicular to the chain backbone, respectively.[15,16] Therefore, from the differential absorption of the bands to IR radiation polarized in orthogonal directions, the mean orientation of chain backbone may be deduced and its time dependence may be studied in situ.

Experimental Section

Dichroism Measurement. Infrared spectra were collected in the mode of attenuated total reflection (ATR) using a Bio-Rad FTS-60 Fourier transform infrared spectrometer (FTIR). The ATR crystal, a rectangular trapezoid composed of germanium (Ge), had a 45° angle of incidence. It was mounted in a cell, described elsewhere,[8] designed to allow the solution to contact the Ge surface and to allow the rapid replacement of polymer solutions. The Ge surface was oxidized in a controlled fashion, by exposure to oxygen plasma, using the same methods developed previously for the oxidation of silicon.[8] These methods of surface preparation were found to give a stable surface such that adsorption measurements could be reproduced quantitatively from experiment to experiment.

In ATR optical geometry, the optical beam propagates within the crystal, totally reflects at the crystal surface, and forms an evanescent field on the solution side. For the measurement of dichroism, the incident beam was polarized in the p-direction (parallel to the incident plane) or s-direction (perpendicular to the incident plane), and the absorbances in both polarization directions (A_p, A_s) were measured. The

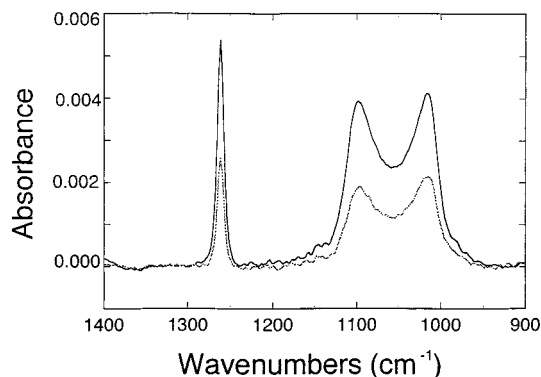† Permanent address: Mitsubishi Chemical Corporation, Yokohama, Kanagawa 227, Japan.

Figure 1. Infrared spectrum of PDMS adsorbed onto Ge crystal surface from carbon tetrachloride solution of concentration 0.49 mg mL^{-1}. The solid line shows the spectrum taken with a p-polarized beam (electric field parallel to the incident plane), and the dotted line shows the spectrum taken with an s-polarized beam (electric field normal to the incident plane).
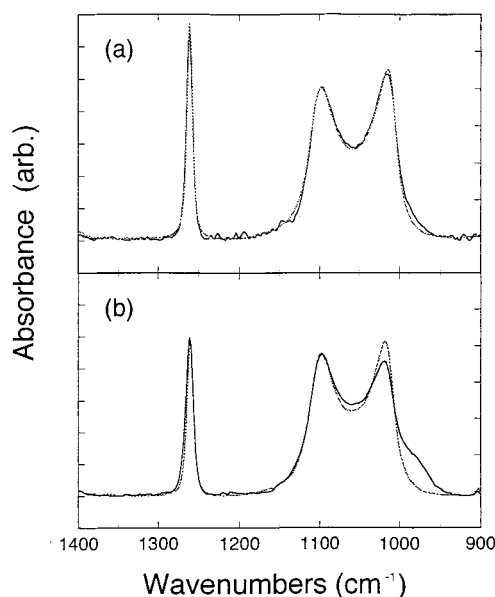

Figure 2. Comparison of spectra in free solution and in the adsorbed state (measurements taken with unpolarized radiation). The solvent is carbon tetrachloride (panel a) and cyclohexane (panel b). The solid lines indicate spectra of PDMS adsorbed onto an oxidized Ge crystal from solution; the dotted lines indicate spectra in transmission.

components of the absorbance at the crystal surface (the components in each of the three orthogonal Cartesian directions) were derived from A_p, A_s, the angle of incidence, and the refractive indices of solvent and crystal, by established formulas.[19]

To simplify the situation, we assumed that the real parts of the refractive indices were isotropic and that the imaginary parts were negligibly small. We also assumed that there was no preferential orientation in the plane of the solid surface, namely $A_x = A_y$ (here x and y are the Cartesian coordinates in the plane of the surface, and the coordinate z is normal to it). This gave the dichroic ratio, $D \equiv A_z/A_x$, the ratio of vertical and horizontal components of a dipole moment. For example, if all dipole moments of a specific functional group were oriented within the horizontal plane, D of that group would be zero. The larger the vertical component, the larger the D value. For an isotropic random distribution of orientations, as in solution, D is unity.

Samples and Procedure. Poly(dimethylsiloxane) (M_w =118 000 and M_w/M_n = 1.16) was purchased from Polymer Source, Inc. (Montreal). Carbon tetrachloride was purchased from Aldrich and used as received. The interaction between the PDMS segment (its ether group) and Ge oxide is expected to be strong in analogy to the known segment-surface interaction energy of $5.1k_BT$ between poly(ethylene oxide) (PEO) and the silica surface[20] (here k_B is the Boltzmann constant and T is the absolute temperature).

To initiate the experiments after mounting the oxidized germanium crystal into the adsorption cell, carbon tetrachloride solvent was introduced into the cell. After stabilizing for 4 h, background spectra were collected for both p- and s-polarization, and then solvent was replaced by PDMS solution. Temperature was controlled at 25.0 °C throughout the experiments. The ATR intensity (A_p and A_s) of each specific band was measured in situ, for both p- and s-polarization alternately, by switching a wire-grid polarizer. Thus the s and p spectra were measured at slightly different times. To determine the absorbance at a specific time, A_p and A_s at that time were obtained by interpolation. In some experiments the solution was again replaced by carbon tetrachloride solvent after allowing some amount of adsorption to see adsorbed layer changes without later-arriving polymer chains. As a matter of terminology, we define "surface excess" as the mass per unit area, in excess of that attributable to bulk solution, within the volume sampled by the evanescent infrared radiation.

Results and Discussion

PDMS Spectrum. Figure 1 shows an ATR spectrum of PDMS adsorbed onto oxidized Ge from carbon tetrachloride solution. A sharp peak at 1261 cm^{-1} is assigned to the Si$-$CH$_3$ symmetric bending mode. The

dipole moment of this band is perpendicular to PDMS backbone and was previously used to determine segmental orientation of PDMS networks.[15] A strong band located between 1000 and 1150 cm^{-1} is assigned to Si$-$O$-$Si stretch vibrations. This band includes at least two strong peaks. Tsao and Rabolt assigned these peaks to asymmetric and symmetric Si$-$O$-$Si stretch absorbance from calculations based on Hartree$-$Fock theory.[16] Their calculations assign the band at higher wavenumber to the symmetric stretch whose dipole moment is perpendicular to the PDMS backbone and the band at lower wavenumber to the asymmetric stretch, whose dipole moment is parallel to the PDMS backbone.

In the following discussion we emphasize the asymmetric Si$-$O$-$Si stretch. In this case, orientation of the dipole moment directly matches the orientation of the PDMS backbone and is easiest to analyze. The IR bands having a dipole moment perpendicular to the backbone also give useful information about polymer orientation, but their dichroic ratio was also affected by radial distribution of dipole moment. This is not considered to be uniform at the surface because of preferential adsorption of oxygen atoms to the surface.

Figure 1 also compares p and s polarization spectra. For further analysis of the data, the integrated absorbance intensity of each band was derived from curve-fitting. After the calibrated contribution from free polymers in the solution was subtracted, as described elsewhere,[7,17] vertical and horizontal absorbances were calculated from those data. Then both the dichroic ratio and the total absorbance of each band were determined. Total absorbance can be converted to an adsorption mass amount by calibration experiments.[17] In Figure 2a, PDMS spectra in a carbon tetrachloride solution and in an adsorbed layer on Ge from carbon tetrachloride solution are compared. Intensity is normalized by the Si$-$CH$_3$ band which is supposed to be less sensitive to adsorption stimulated changes. In the spectrum of the adsorbed layer, a small shoulder is observed around
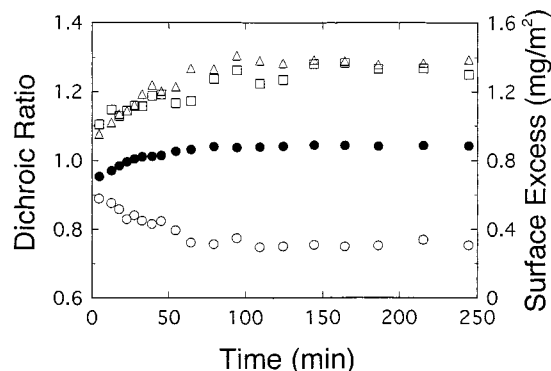
Figure 3. Time evolution of dichroic ratio and surface excess of PDMS as it adsorbed onto oxidized Ge from carbon tetrachloride solution of concentration 0.49 mg mL^{-1}. Open circles show the dichroic ratio of the Si−O−Si asymmetric stretch band. This band has dipole moment parallel to PDMS backbone. Open squares and open triangles show the dichroic ratio of the Si−O−Si symmetric stretch vibration and the Si−CH$_3$ symmetric bending vibration, respectively. Dipole moments of these two bands are nearly perpendicular to the polymer backbone. Filled circles denote the surface excess.

960−1000 cm^{-1}, which does not appear in the solution. This shoulder is seen to be much clearer and larger, when one compares a spectrum in a cyclohexane solution and a spectrum of adsorbed PDMS from a cyclohexane solution, as shown in Figure 2b. In cyclohexane the adsorbed amount is almost twice as large as in carbon tetrachloride, and we expect this to reflect more bound segments, i.e., segments that are hydrogen-bonded to the surface.[18] From these results we suppose that this peak comes from a bound siloxane band. We use it for bound fraction discussion. However because of uncertainty about the molar absorptivity (for example, the molar absorptivity of the carbonyl group increase 50% upon hydrogen bonding to a surface[7]), we focus on time dependence of the ratio of the bound peak to the total peak and do not discuss the exact bound fraction value.

Orientation and Relaxation at the Surface. Orientation changes during adsorption were first studied during the course of adsorption onto an initially bare surface. Figure 3 shows the time evolution of both the dichroic ratio and the surface excess during adsorption from 0.5 mg mL^{-1} carbon tetrachloride solution. This concentration is dilute (i.e. less than semidilute). The dichroic ratio of three different bands is shown. The dichroic ratio derived from the Si−O−Si asymmetric stretch has dipole moment parallel to the PDMS backbone. The dichroic ratio derived from the Si−O−Si symmetric stretch and the Si−CH$_3$ symmetrical bending band reflects dipole moments perpendicular to the PDMS backbone. In Figure 3, we observe that the time evolution of the Si−O−Si symmetric band showed changes similar to those of the Si−CH$_3$ band. On the other hand changes of the Si−O−Si asymmetric band were in the opposite direction. This supports the dipole moment assignment discussed in the previous section. In the following discussion we focus on the dichroic ratio of the Si−O−Si asymmetric band. The dipole moment of this band is parallel to the PDMS backbone, so the dichroic ratio of this band directly showed the average orientation of the PDMS backbone and made it easier to understand the PDMS conformation at the surface.

At the very initial stage of the adsorption the dichroic ratio was about 0.9. This means that at the solid

surface the directional distribution of PDMS backbone was no longer isotropic, as when free in a solution, but had a slight preference toward horizontal alignment. Thus we interpret this to signify that adsorbed PDMS took a flattened shape on the surface. As adsorption continued, the dichroic ratio gradually decreased for about 2 h. Therefore, it is supposed that the adsorbed polymers continued to change their average shape to a more flattened one. For homopolymer adsorption the adsorbed polymer shape can be expected to spread onto the surface with some degree of segment−surface adsorption energy. In the flattened conformation more segments can be attached to the surface, and this can reduce the total energy of adsorbed polymers. This can be a driving force for flattening, and it occurs not only for isolated adsorbed polymer coils but also for polymers within the adsorbed layer. At steady state the dichroic ratio attained the value of 0.75. This value is similar to but a little larger than that for poly(ethylene oxide) adsorbed from aqueous solution ($D = 0.6$).[21] The difference may reflect the solubility difference of PDMS carbon tetrachloride solution and PEO water solution or a difference of surface affinity.

We can discuss the adsorbed polymer properties further by considering the adsorbed amount, which is also shown in Figure 3. At first the adsorbed amount quickly (within a period less than one minute) reached 0.7 mg m^{-2}, 70% of its final value, and the dichroic ratio took the value of 0.9. At this relatively high surface coverage, one might expect the adsorbed chains to be crowded and to tend to extend from the surface, so it is surprising that PDMS backbone still showed net horizontal orientation. The process from zero to this stage depended on the details of how the solution was introduced to the sample surface and could not be measured precisely with the current system. At lower adsorbed amounts, it is considered probable that the polymer deposited more freely onto the surface and that the rate was controlled by convection and diffusion of polymer to the surface, but we will not discuss this process here. We just mention that after the point was reached of 70% of the final adsorption value, subsequent adsorption events within this dense layer proceeded exceedingly slowly. Prior work from this laboratory concerning the displacement kinetics of chains of low molecular weight by other chains of higher molecular weight shows these kinetics to be even more sluggish,[8,9] so an explanation in terms of residual molecular weight distribution in the polymer sample seems unlikely. We seek explanation instead in slow conformational rearrangements in the adsorbed state.

As the adsorbed amount increased for 2 h, the dichroic ratio continued to decrease. It is worth emphasizing that there was correlation between the increase of adsorbed amount and the decrease of dichroic ratio. In general a later-arrived polymer could not find enough space to adsorb or spread on the surface, especially in the condition where the adsorbed amount already exceeded 70% of its steady-state value. So it is natural that later-arrived polymers adopted a less flattened conformation at the surface and raised the average dichroic ratio value. From these results it is considered that two process occurred simultaneously: flattening of the already-adsorbed polymers and adsorption of later-arriving ones. We also suppose that the adsorbed polymer relaxation to a spread conformation canceled out the tendency of later-arrived polymer to raise the
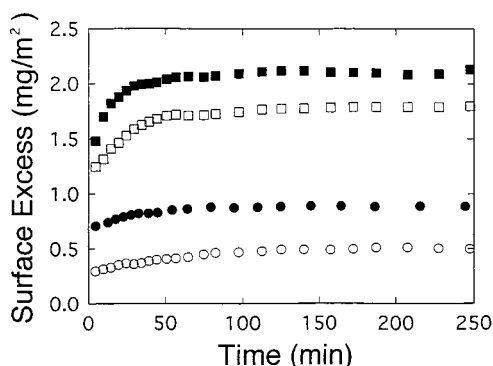
Figure 4. Time evolution of the surface excess as PDMS adsorbed onto initially bare oxidized Ge from solutions of various concentration. Key: open circles, 0.20 mg mL^{-1}; filled circles, 0.49 mg mL^{-1}; open squares, 1.30 mg mL^{-1}; filled squares, 3.06 mg mL^{-1}.
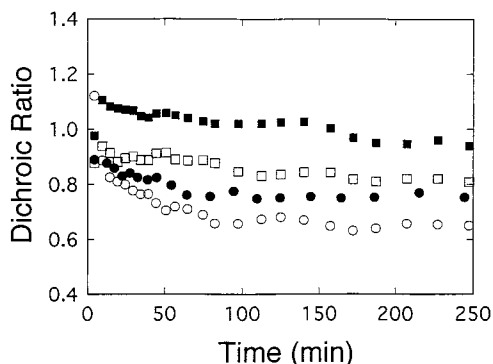

Figure 5. Time evolution of the dichroic ratio of the Si$-$O$-$Si asymmetric stretch (dipole moment parallel to PDMS backbone) for the same experiments shown in Figure 4. Symbols are the same as in Figure 4.

dichroic ratio. The adsorbed polymer flattening also reduced osmotic pressure between chains within the adsorbed layer and gave some space for additional polymers to adsorb. This can explain the correlation of the dichroic ratio and the adsorbed amount. Without those later-arrived polymers, the conformation change of the adsorbed polymer might be larger than it was observed here, and we will discuss this later.

Dependence on Solution Concentration. The same type of experiments as just discussed were also performed at other solution concentrations and gave some information about the adsorbed amount contribution to the relaxation process. In Figure 4 the time evolution of surface excess at various concentrations is shown, and Figure 5 shows the time evolution of the dichroic ratio of the asymmetric stretch band for the same experiments.

In Figure 4, one notices concentration dependence of the adsorbed amount for concentrations up to about 3 mg mL^{-1}. From other experiments it was found that the adsorbed amount reached a plateau region around this concentration. Concerning the time dependence, the curves show more or less the same pattern at each solution concentration as at 0.5 mg mL^{-1}. But there are some differences. When normalized by the steady-state value, the initial amount was larger, the larger the solution concentration. And the rate of subsequent increase was also faster. This means there was still some concentration dependence about the adsorption process, though the increase rate itself was much slower than one could expect from a process whose rate was controlled by diffusion through a solution.

The time and the concentration dependence of the dichroic ratio (Figure 5) are also very suggestive. Here it is clear that at the higher concentrations the dichroic ratio was higher than at low. It ranged from 0.9 to 1.1 at the initial stage and from 0.65 to 0.95 4 h later. At the higher concentrations the adsorbed amount was also higher, and from equilibrium state studies it is considered that the crowded adsorbed polymer was forced to take more extended conformations from the surface. This caused the PDMS backbone to be less flattened and gave a higher dichroic ratio.

One interesting point is that the dichroic ratio was always between 0.9 and 1.0 at the start point, regardless of the solution concentration. This initial narrow range supports the idea that the conformation of molecules shortly after adsorption is independent of adsorbed molecule density. Whichever portion of the polymer touches the surface at first, the polymer can subsequently fall down on to the surface and can tend to flatten, which gives maximum adsorbed sites and lowest energy without causing a large distortion of the random coil structure. So before relaxation and extra adsorption are going on, randomly deposited polymers may show little horizontal preference.

Regarding the kinetic aspects, at each concentration, higher or lower, the dichroic ratio decreased with time in the manner discussed above for the 0.5 mg mL^{-1} solution, so the PDMS conformation changed to become more flattened on average regardless of the adsorbed amount. But the time dependence was not the same. The rate of change was faster at lower concentrations, such as in 0.20 and 0.49 mg mL^{-1}, for the first 1 or 2 h. Then 2 or 3 h later the dichroic ratio reached a steady value for those concentration solutions. At this point the adsorbed amount also reached an almost stable value. On the other hand at higher concentrations such as 1.3 and 3.0 mg mL^{-1}, the rate of dichroic ratio change was slower and kept decreasing even after 4 h. In these cases the adsorbed amount reached steady-state values within 1 h. Taken together, the data show that the dense layer rendered the relaxation slower but that flattening still occurred in such thick adsorbed polymer layers.

Bimodal Distribution of Conformations. The dependence of the dichroic ratio on the adsorbed amount seems very natural, but the structure of the adsorbed layer may be more difficult to elucidate from the results.

The high dichroic ratio during the initial adsorption supports the idea that the conformation is different at early stages of association with the substratum that at later stages of contact and is independent of the concentration in solution. As the surface coverage grows and adsorbed chains become crowded, it is reasonable to expect segments of the chains to be expelled from the surface. Two scenarios can be imagined. One possibility is that all polymers more or less equally contribute to stretched-out conformations. In this case each polymer would occupy a lesser area and extend in the vertical direction somewhat like a polymer brush. Another possibility is that some partial fraction of the total population of polymers would take such a role. By this picture some polymers would adsorb tightly while some would be expelled and consequently be loosely adsorbed, overlapping the tightly adsorbed one.

While the adsorbed amount is still increasing, the latter apparently occurs. The later-arrived polymer
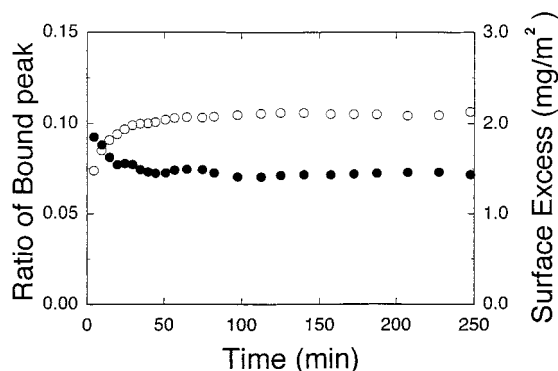
Figure 6. Time evolution of the ratio of bound peak intensity to total intensity of the asymmetric Si−O−Si peak during adsorption from a carbon tetrachloride solution of 3.06 mg mL^{-1} (filled circles). Open circles show the associated surface excess at each time.

Figure 7. Comparison of the time evolution of surface excess in pure solvent after a brief adsorption time (filled circles; see explanation below), and in continuous exposure to 1.3 mg mL^{-1} solution (open circles). For the case of pure solvent, first the solution was introduced and PDMS was allowed to adsorb for about 10 min, and then the solution was replaced to pure carbon tetrachloride.

Figure 8. For the same experiment shown in Figure 7, dichroic ratios of Si−O−Si asymmetric stretch of adsorbed PDMS (dipole moment parallel to the PDMS backbone) are plotted against time. Symbols are the same as in Figure 7.

finds less free surface and so adsorbs more loosely with fewer adsorbed sites. This interpretation is also supported by the bound fraction data. Figure 6 shows the time dependence of the ratio of bound segments (cf. Figure 2b) to the total intensity of the asymmetric peak. This ratio is, we suppose, related to the bound fraction. The unbound peak intensity increased with time in the same manner as the adsorbed amount, which is also shown in Figure 6. In contrast, the bound peak saturated almost immediately and showed only a small increase. So we see that the ratio of bound segments decreased with time, as the adsorbed amount increased. This means that the later-arrived polymers had fewer adsorbed sites. This same feature was also observed in poly(methyl methacrylate) adsorption onto oxidized silicon.[8] From these studies we can conclude that at first the adsorbed layer is comprised of two types of adsorbed polymers, loosely adsorbed and more fixed.

Then the relaxation process continues in the layer—to which type of structure does it tend? At the end of the immersion in 0.5 mg mL^{-1} solution the adsorbed amount was 0.89 mg-m^{-2}, with dichroic ratio 0.76. If all adsorbed polymers took similar conformations, we could roughly evaluate an occupied area per one polymer from the dichroic ratio, the bond length, and the molecular weight. The resulting calculated diameter is around 46 nm, which gives an adsorbed amount of 0.12 mg mL^{-1}. The observed adsorbed amount is much higher, and this (if the adsorbed layer were conformationally homogeneous) would imply that the chains should be extended normal to the surface with a dichroic ratio larger than unity. However, the observed dichroic ratio is less than unity, so it is not plausible that uniform conformation could be consistent with the observed dichroic ratio and adsorbed amount.

On the other hand, assuming that some amount of polymer took an isotropic conformation, namely loosely adsorbed, the dichroic ratio can be explained better. The adsorbed amount difference was 1.22 mg mL^{-1} between 0.5 and 3.1 mg mL^{-1} solution concentrations. If we add the difference as an isotropic conformation one, we can rationalize the dichroic ratio in 3.1 mg mL^{-1} solution from the observed dichroic value, 0.76, in 0.5 mg mL^{-1} solution. The prediction is 0.89, to be compared with the measured value 0.95. Because relaxation is known to be slow within the dense layer, the predicted dichroic ratio may be enhanced, and this may be a reasonable estimate.
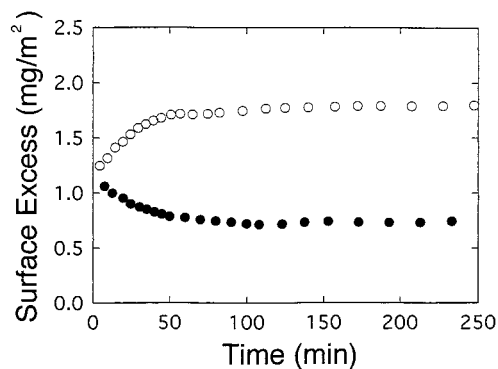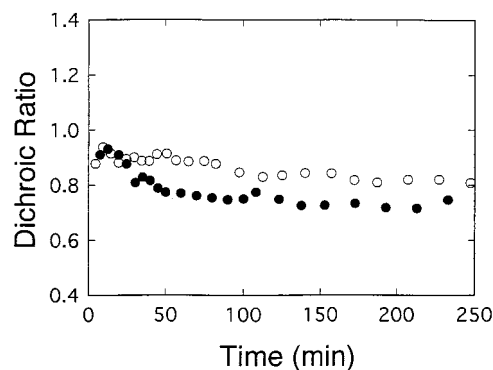
So we suppose that the adsorbed layer was comprised of two distinct types of conformations. One was flattened and tightly bound to the surface, and the other was loosely adsorbed with fewer adsorbed segments. As the adsorbed amount increased, the percentage of this loosely adsorbed polymer increased and raised the total dichroic ratio while lowering the bound fraction. This view could also explain the adsorbed amount variation with solution concentration. We suppose that the increase of adsorbed amount in the concentration range of our experiment reflected contributions from loosely adsorbed polymer.

Relaxation processes without later arrived polymer also gave a suggestive result. Figures 7 and 8 compare the time evolution of the relaxation process in solution and in pure solvent. In the pure solvent experiment, PDMS solution was introduced to allow PDMS to adsorb onto the Ge surface at first. Then after about 10 min immersion time, the solution was replaced by the pure carbon tetrachloride solvent.

In the solvent the adsorbed amount decreased with time, and after approximately 2 h, it reached a steady value. This was 43% of the adsorbed amount from solution. So some polymers, which adsorbed to the surface from solution, desorbed when exposed to the pure solvent. This result also suggests that there existed some weakly adsorbed polymers and a distribution of adsorption states. Regarding the desorption driving force, there might be several possibilities. One

possibility is a concentration effect. Loosely adsorbed polymer which was in an equilibrium state may desorb, in solvent, to reach a new equilibrium state. The other possibility is a polymer conformational rearrangement within the adsorbed layer. When one polymer spreads on the surface, it occupies more sites and repels neighbor polymers by steric repulsion and occupation of adsorption sites. The observed concentration dependence of the adsorbed amount supports the former process, while the observation of dichroic ratio decrease even during adsorption from solution shows that rearrangement process surely took place. In this experiment it is not sure which part dominated.

The dichroic ratio decreased with time both in solution and solvent, but in solvent it was always lower for uninterrupted adsorption from solution. Figure 8 also shows that the decrease rate was somewhat faster in pure solvent, especially within the first hour after the replacement. This may reflect primarily the loss of weakly adsorbed polymers that had a less flattened conformation, thus simply lowering the mean dichroic ratio of the remainder. But there is also some possibility that removing polymers from within the layer gave more mobility to the remaining polymers, and enhanced the flattening speed. At 4 h elapsed time, the dichroic ratio reached 0.84 in solution and 0.75 in solvent. The adsorbed amounts were 1.76 and 0.75 mg-m^{-2}, respectively. The polymer making the adsorbed amount difference should have the average dichroic ratio 0.91. So hypothetical combination of 0.91 dichroic ratio polymers on 0.75 mg-m^{-2} base layer in solvent could explain the adsorbed layer in solution. Those simple calculations agree with the previous discussion that also gave the conclusion that the total adsorbed amount included a significant contribution from loosely adsorbed polymer.

Conclusion

We measured the backbone orientation of PDMS adsorbed at a solid surface and evaluated the subsequent relaxation processes within the adsorbed layers. Within the adsorbed layers, the PDMS backbone showed a net orientation horizontal to the surface and continued flattening even as additional chains deposited. The average orientation and time scale of the relaxation process changed when the adsorbed amount was varied.

This is believed to reflect crowding at the surface. The net polymer backbone orientation, derived from infrared active vibrations along the backbone, was found to give useful information about adsorbed polymer conformations. This technique will be additionally useful if some external shear field is applied and generates some directional preference within the plane; studies directed toward measuring shear-induced conformational changes are in progress.[18]

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