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Monomolecular Films of Polydimethylsiloxanes on Organic Liquids

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ABSTRACT

A homologous series of polydimethylsiloxanes was spread as insoluble monomolecular films on water and on a number of organic liquids of varying surface tension and surface composition. The organic liquids studied as substrates were tricresyl phosphate, propylene carbonate, diethylphthalate, bis(2-ethylhexyl)adipate, and hexadecane. Monolayer stability and insolubility were found to vary with the molecular weight of the polydimethylsiloxane and the polarity of the substrate liquid. Stable, reversible monomolecular films were formed on all substrates by the higher-molecular-weight polymers (mol wt > 6000); however, film stability decreased with decreasing polymer molecular weight and decreasing substrate polarity.

The orientation of the polydimethylsiloxane films at the organic liquid/air interfaces depended on the surface composition of the substrate liquids. On tricresyl phosphate and propylene carbonate the high-molecular-weight polymers adsorbed in a fully extended configuration at large areas per molecule, analogous to their behavior on water. With compression they assumed a helical configuration with six monomer units per helix. On the less polar substrates the polydimethylsiloxanes apparently remained in the helical configuration regardless of the state of compression.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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MONOMOLECULAR FILMS OF POLYDIMETHYLSILOXANES ON ORGANIC LIQUIDS

INTRODUCTION

Polyorganosiloxanes and their derivatives are becoming increasingly important as surface-active agents (1,2). They have been studied as soluble surfactants (3,4) and insoluble monomolecular films (5-14) and have been used successfully as waterproofing materials, foaming and defoaming agents, and wetting agents in both aqueous and nonaqueous systems (1,2). As a result of insoluble monolayer studies on water, the behavior of polydimethylsiloxane polymers at aqueous surfaces is reasonably well understood. Few analogous studies have been made of insoluble polyorganosiloxane monolayers on nonaqueous substrates; consequently, little is known about their orientation and structure at the organic liquid/air interface. Banks (7,9) and Ellison and Zisman (8) first reported that polydimethylsiloxanes gave insoluble surface films on organic substrates. Banks found that a polydimethylsiloxane with an average molecular weight of about 2000 gave stable surface films on such organic liquids as oleic acid, olive oil, tri-acetin, and ethylene glycol. Ellison and Zisman, using an ethoxy end-blocked polydimethylsiloxane with a molecular weight of 8250, established that stable monomolecular films were formed on tricresyl phosphate and hexadecane. They also reported that other types of polyorganosiloxanes, such as diethyl, methylphenyl, and methylchlorophenyl, would spread on nonaqueous substrates.

The previous studies of the polyorganosiloxane monolayers on organic liquids indicated that their behavior as surface films would highly depend on the nature of the substrate. The present investigation was undertaken to study in greater detail the properties of insoluble polydimethylsiloxane monolayers on a series of organic liquids and to relate the monolayer behavior to the differences in surface tension and surface composition of the substrate. The monomolecular films were studied using a Teflon film balance trough similar to that described earlier by Zisman and coworkers (8,15). In the present investigation changes in substrate surface tensions were measured using the Wilhelmy plate technique. The film balance was modified for continuous compression of the film and for continuous monitoring of the film pressure.

MATERIALS

A series of polydimethylsiloxanes of the type $(CH_3)_3Si\left[O\,Si(CH_3)_2\right]_x OSi(CH_3)_3$, kindly supplied by the Dow Corning Company, was used in this investigation. Two siloxanes, with x = 10 and 14, were well-defined homogeneous samples. The higher-molecular-weight polydimethylsiloxanes were DC 200 series fluids of 20-cs, 50-cs, 100-cs, and 350-cs viscosity at 25°C. From the relationship between molecular weight and viscosity, it was determined that these polymers had average molecular weights of 1920, 3700, 6100, and 15,000. This would correspond to average values of x = 23.7, 47.7, 80.2, and 207, respectively. To remove surface-active impurities, the lower viscosity siloxanes, which would readily pass through an adsorption column, were percolated through a column of activated Florisil. Petroleum ether (bp = 41-55°C) from Fisher Chemical Company and Freon TF (bp = 47.6°C) from E.I. du Pont de Nemours and Company were used as spreading solvents. Before use these solvents were also passed through adsorption columns containing activated Florisil.

In addition to water ($\gamma_{20°}$ = 72.6 dynes/cm), the following organic liquids were used as substrates: tricresyl phosphate ($\gamma_{20°}$ = 40.7 dynes/cm), propylene carbonate ($\gamma_{20°}$ = 41.0 dynes/cm), diethylphthalate ($\gamma_{20°}$ = 36.0 dynes/cm), bis(2-ethylhexyl)adipate ($\gamma_{20°}$ = 29.6 dynes/cm), and hexadecane ($\gamma_{20°}$ = 27.6 dynes/cm), all from the Eastman Organic Chemical Company. Distilled water from a tin-lined Stokes still was further purified by putting it through a two-stage all-quartz Heraeus distillation apparatus. Propylene carbonate, diethylphthalate, bis(2-ethylhexyl)adipate, and hexadecane were percolated through Florisil, while the more viscous tricresyl phosphate was used as received. All spreading solutions were delivered to the substrate surfaces from microliter syringes obtained from the California Laboratory Equipment Company.

EXPERIMENTAL TECHNIQUE

The Teflon film balance used in these experiments was similar to those described earlier (8,15), except that the Langmuir-type float and torsion head described by Ellison and Zisman (8) to measure changes in the film pressure (F) were replaced by a Wilhelmy plate. This avoided the problem of monolayer leakage through the openings between the ends of the Teflon-coated float and the sides of the trough. Elimination of the torsion head also made it easier to sweep a film from the surface of the substrate at the conclusion of a run. It was still necessary to use small nitrogen gas jets as described previously (8,15) to confine the film at the ends of each movable barrier.

The Wilhelmy plate was made of platinum, which was 3.35 cm long, 1.5 cm high, and 0.005 cm thick, with the surface roughened with a 400A grit silicone carbide paper to improve wetting. The plate was attached to a Statham UC2 strain gage and a UR5 transducer readout. The signal was recorded continuously on a Varian G-11A recorder. During most of the experimental runs the sensitivity was adjusted so that each division on the chart paper corresponded to 0.10 dyne/cm. Film-pressure differences of 0.02 dyne/cm could be easily read from the chart paper. The movable Teflon barriers were coupled with a variable speed motor drive to permit continuous compression of the adsorbed film. The rate of compression used with a particular substrate varied with the length of time required for the film to reach equilibrium. For monolayers that were apparently unstable, whose film-pressure-vs-area (F-vs-A) curves depended on the barrier compression rate and the initial surface concentration of polymer, a standard rate of compression of 1/3 cm per minute and a constant initial surface concentration were used to give reproducible results. The film balance and strain gage were enclosed in a Lucite box during the runs to maintain a dust-free atmosphere. The experiments were carried out in an air-conditioned room where the temperature was maintained at 23° ± 1°C.

Spreading solutions of the siloxanes were prepared by dissolving known amounts in petroleum ether or Freon TF. Both spreading solvents have some solubility in the organic liquids, but inasmuch as they are very volatile and spread rapidly over each substrate to form thin films, the rates of evaporation should be rapid and little solvent apparently remains to interfere with the monolayers. This appeared to be true, because solutions of a given siloxane prepared in each solvent gave the same curve of F-vs-A per molecule, and increasing the solvent content from 0.050 ml per monolayer to 0.250 ml per monolayer did not significantly affect the F-vs-A curve. Freon TF, having a somewhat lower surface tension and forming smaller droplets at the tip of the syringe, appeared to give more reproducible results and was used as the spreading solvent in most experiments on organic liquid substrates. However, petroleum ether was the spreading solvent used for all experiments with monolayers on water.

Before beginning a series of runs on a new substrate, the Teflon trough was cleaned by soaking it overnight in 3:1 sulfuric acid-nitric acid solution, rinsing it profusely with running tap water and then distilled water, and allowing it to dry. The trough was then

flushed several times with the liquid to be used as substrate. The nitrogen-jet-equipped barriers were used to sweep the surface of the substrate free from adsorbed impurities. A suction device was placed at the end of the tray to remove the impurities trapped by the barriers. Prior to use, the nitrogen gas was passed through an adsorption column containing activated charcoal. The Wilhelmy plate, cleaned by heating to red heat, was then lowered until it just touched the substrate surface, and the recorder pen was adjusted to indicate zero film pressure. After several minutes the spreading solution was added dropwise, each drop being touched gently to the surface, with sufficient time allowed for equilibrium to be attained. The barrier was set in motion, and changes in film pressure were recorded as a function of the surface area. Depending on the rate at which a monolayer reached equilibrium on a given substrate, the time necessary to complete a run varied from about 2 to 4 hr.

The stability of the polydimethylsiloxane monolayers was determined by allowing them to remain at high film pressure at the end of the compression run and observing any decrease in film pressure with time. If the monolayer was unstable, or the polydimethylsiloxane somewhat soluble in the substrate, a significant decrease in film pressure was detected after several minutes. Film stability was also determined by measuring the F-vs-A expansion curve, as well as the compression curve, and noting the amount of hysteresis. Because of the length of time required to complete both a compression and an expansion run, expansion curves were determined only once for each polydimethylsiloxane on the various substrates. The contact angle of the substrate on the platinum plate appeared to remain zero during the course of each reported run. At the completion of a run, the Wilhelmy plate was removed from the surface and the adsorbed film swept to the end of the tray where it was removed by suction. The sweeping procedure was repeated six or seven times, a new substrate was added, and a new run was begun. The substrate in the tray was replaced daily to insure no accumulation of contamination.

RESULTS

Isotherms of F-vs-A per molecule were determined for the six polydimethylsiloxanes on each organic substrate as well as on water. The F-vs-A curves of all the polymers were repeated at least five times and in most instances were reproducible within ±0.2 dyne/cm. The stability of the monomolecular films varied with the molecular weight of the polymer and the nature of the organic substrate. All films studied were stable and insoluble on water and tricresyl phosphate, showing no change in film pressure on standing 30 min at the smallest area per molecule.

The polydimethylsiloxane films were also quite stable on propylene carbonate; only the decamer was appreciably unstable, losing a few tenths of a dyne film pressure in 30 min at maximum compression. The polymers were considerably more soluble in diethylphthalate; those with 14 or fewer repeating units per molecule rapidly lost film pressure on standing at closest packing. Monolayers of the tetradecamer lost approximately 1 dyne/cm in only 12 min. On bis(2-ethylhexyl)adipate and hexadecane polymer monolayers of even the highest molecular weight showed measurable instability, losing 0.4 to 0.6 dyne/cm after 30 min at the lowest reported areas per molecule. The apparent instability of the polydimethylsiloxanes on hexadecane and bis(2-ethylhexyl)adipate increased with decreasing molecular weight until with the decamer and tetradecamer it was difficult to determine meaningful F-vs-A curves due to the rapid loss of film pressure. Monolayer instability in each case was believed to be due to solubility of the polymers.

In Fig. 1, the F-vs-A curves are given for the 47 repeating-unit polydimethylsiloxane ($x = 47$) on each substrate. The points on each curve were taken from the recorder tracing of a single representative run. Rather than present the monolayer data for the other

polydimethylsiloxanes as F-vs-A per molecule, they were recalculated and plotted in Fig. 2 as F-vs-A per monomer. Plotting as area per monomer facilitates comparison and interpretation of the data.

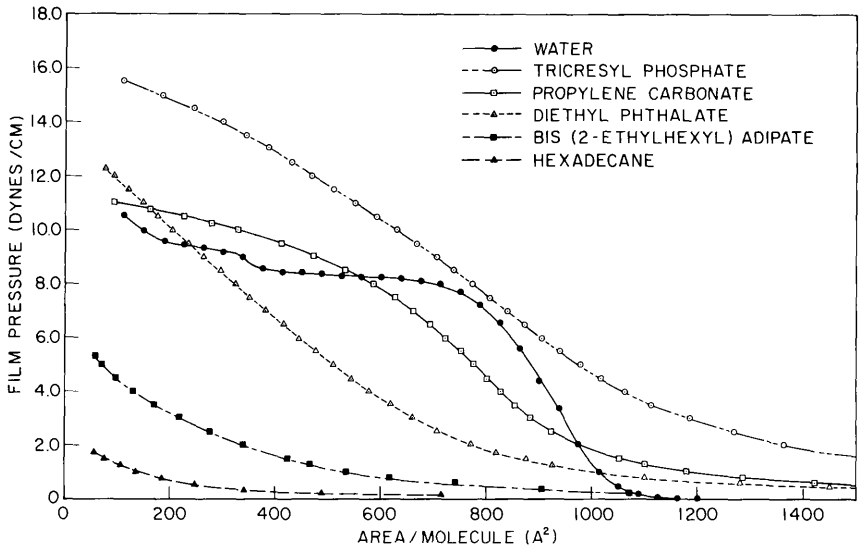
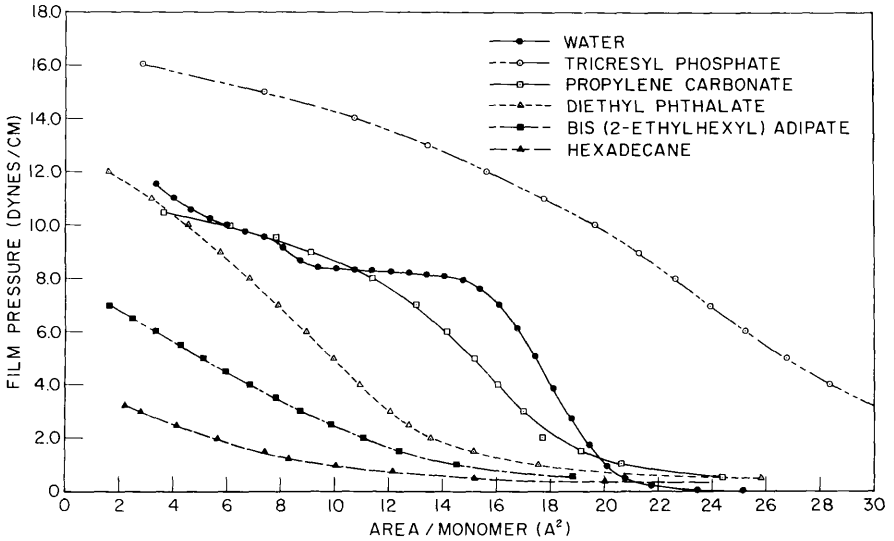


Fig. 1 - Film-pressure-vs-area-per-molecule isotherms for $(CH_3)_3\ Si\left[O\ Si(CH_3)_2\right]_{47.7} O\ Si(CH_3)_3$ on organic liquids

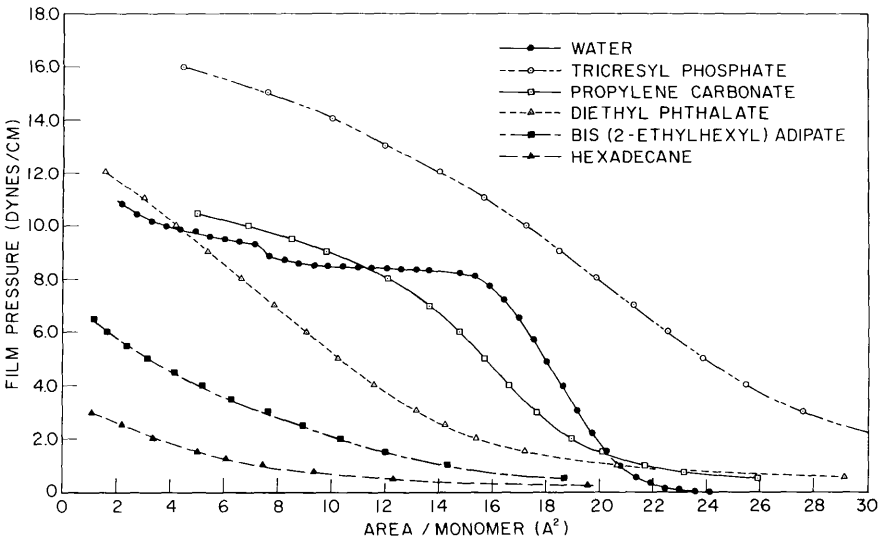
The polydimethylsiloxanes that gave stable monolayers showed little hysteresis in their F-vs-A curves. Figure 3 shows a compression and an expansion curve for the highest-molecular-weight polymer on diethylphthalate. The expansion curves were usually displaced toward lower film pressures than the compression curves but seldom by more than 0.5 to 0.7 dyne/cm. With monolayers on tricresyl phosphate, however, the expansion curves were most often at slightly higher film pressures, possibly due to the length of time required for monolayers to equilibrate on this viscous substrate.

The F-vs-A curves of the polydimethylsiloxanes on water were in excellent agreement with previously reported determinations (5,6,10-14). Only the F-vs-A measurements by Ellison and Zisman (8) and Banks (7) are available for comparison with the present data on organic liquids. Ellison and Zisman (8) reported an F-vs-A isotherm for a polydimethylsiloxane (x = 110) on hexadecane. Their curve showed two sharp discontinuities, which were not observed in the present experiments. When the data of Ellison and Zisman were plotted to the scale of the present experiments, and a smooth curve drawn through them, the two sets of data agreed within a few tenths of a dyne/cm, although the present data extended to a somewhat higher film pressure.

It should be noted that the F-vs-A data in this report were taken by a continuous compression of the film, whereas the previous data were taken by compressing the film in increments, allowing a certain equilibration time after each compression. Considering the instability (or solubility) of the polydimethylsiloxane films on hexadecane, the possibilities that exist for film leakage and the differences in technique, the results are in reasonably good agreement. It is suggested that the sharp discontinuities are experimental artifacts and that the more accurate description of the monolayer behavior is a smooth F-vs-A curve.

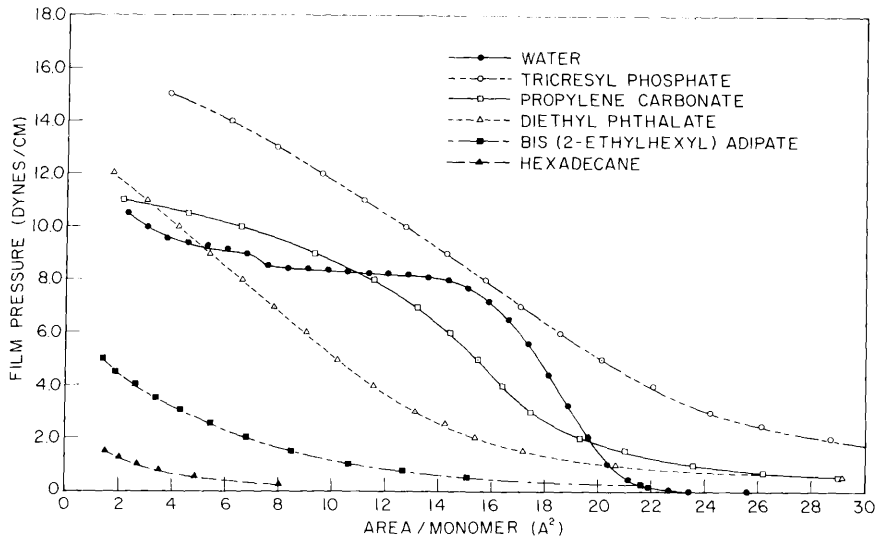


(a) $(CH_3)_3Si\left[O\ Si(CH_3)_2\right]_{207}O\ Si(CH_3)_3$

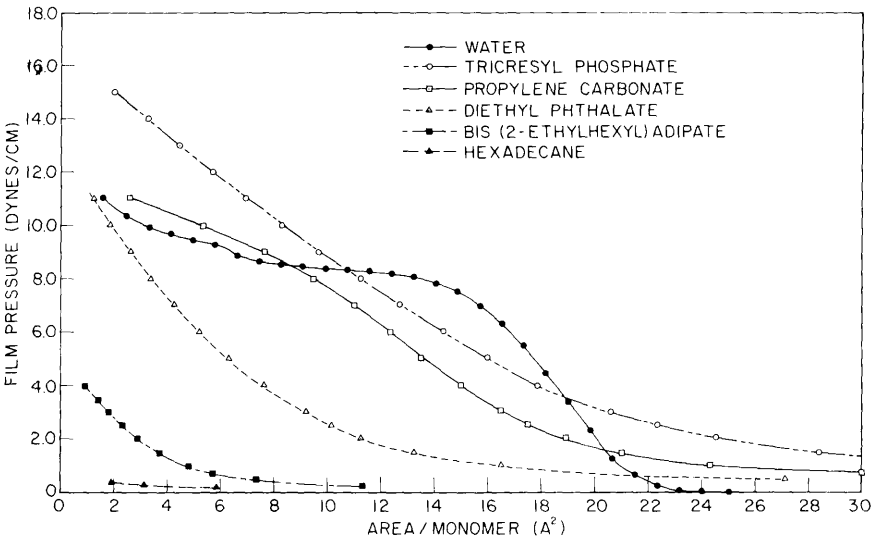


(b) $(CH_3)_3Si\left[O\ Si(CH_3)_2\right]_{80.2}O\ Si(CH_3)_3$

Fig. 2 - Film-pressure-vs-area-per-monomer isotherms of polydimethylsiloxanes on organic liquids

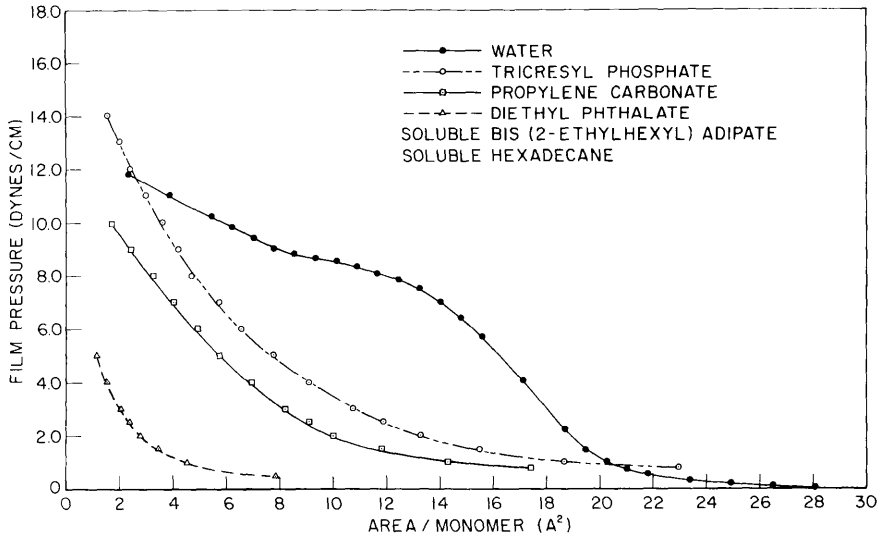


(c) $(CH_3)_3Si\left[O\,Si(CH_3)_2\right]_{47.7}O\,Si(CH_3)_3$

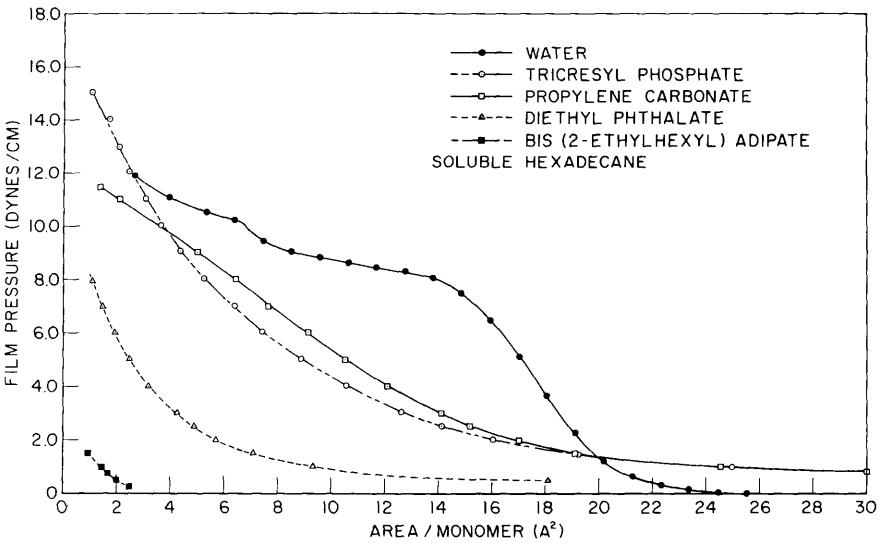


(d) $(CH_3)_3Si\left[O\,Si(CH_3)_2\right]_{23.7}O\,Si(CH_3)_3$

Fig. 2 (Continued) - Film-pressure-vs-area-per-monomer isotherms of polydimethylsiloxanes on organic liquids



(e) $(CH_3)_3Si\left[O\ Si(CH_3)_2\right]_{14}O\ Si(CH_3)_3$



(f) $(CH_3)_3Si\left[O\ Si(CH_3)_2\right]_{10}O\ Si(CH_3)_3$

Fig. 2 (Continued) - Film-pressure-vs-area-per-monomer isotherms of polydimethylsiloxanes on organic liquids

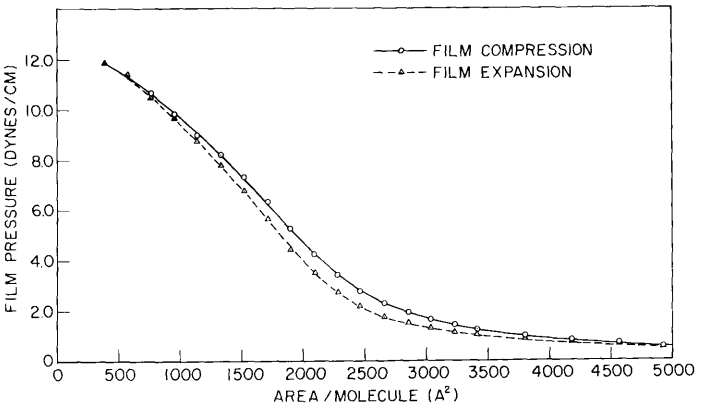


Fig. 3. Hysteresis in film-pressure-vs-area-per-molecule isotherm of $(CH_3)_3Si[OSi(CH_3)_2]_{207}OSi(CH_3)_3$ on diethylphthalate

The isotherms given by Banks (7) were for polydimethylsiloxanes on polar substrates other than those reported here and were determined by adding small increments of the polymer to the substrate to increase surface concentration. In spite of the differences in technique and substrates used, there were many similarities in the two sets of F-vs-A data. As regards the more polar organic liquid substrates, the polymer F-vs-A curves showed many points of similarity with the F-vs-A curves on water.

The F-vs-A isotherms on tricresyl phosphate were particularly interesting. Monolayers of the high-molecular-weight polydimethylsiloxanes were considerably more expanded than on water and gave stable film pressures as high as 16 dynes/cm, well above the film pressure of similar polymers on water at the same area per molecule. Ellison and Zisman (8) in their preliminary study of a monolayer of a polydimethylsiloxane (x = 110) spread on tricresyl phosphate also reported the F-vs-A curve to be more expanded than on water, although not quite to the same extent. By extrapolation they found a limiting area per monomer of 24 Å^2, compared with 21 Å^2 on water. In the present report a limiting area per monomer of 29 to 30 Å^2 was observed for a polydimethylsiloxane having 80.2 monomer units. Ellison and Zisman, however, did not report stable film pressures greater than about 4.5 dynes/cm, compared to the 16 dynes/cm reported here. Their lower film pressures and less expanded films indicate they may have had some difficulty confining the monolayers with the gas jets, particularly at high film pressures.

With decreasing polymer chain length the F-vs-A curves on tricresyl phosphate were relatively less expanded. The decamer and tetradecamer monolayers were more condensed than on water and were similar to the films on propylene carbonate. Even though the high-molecular-weight polymers did not show horizontal plateaus in their F-vs-A curves on tricresyl phosphate and propylene carbonate, they did show a marked decrease in slope at high film pressure.

The decrease in substrate surface tension ($\Delta\gamma$) resulting from the compression of insoluble polydimethylsiloxane monolayers to 3 Å^2 per monomer is given in Table 1 for each substrate liquid studied. With the present experimental apparatus this is approximately the minimum area per monomer that can be obtained and still have the polymer molecules fully extended at the beginning of each run. More compact films of polydimethylsiloxanes on water have been reported to give film pressures of 20 dynes/cm or more; however, they were somewhat unstable (5,13). Other than on water, the order of increasing

$\Delta\gamma$ shown in Table 1 would probably remain the same with further monolayer compression, since the surface tensions in most cases are roughly the limiting value, that of the pure polydimethylsiloxane ($\approx$ 20 dynes/cm at 20°C).

Table 1
Surface Tension Lowering of Organic Liquids by an Insoluble Monolayer of Polydimethylsiloxane (mol wt = 15,000) at 3 Å^2 per monomer

Substrate	(a) Initial Substrate Surface Tension (dynes/cm)	(b) Film Pressure ($\Delta\gamma$) at 3 Å^2 per monomer (dynes/cm)	(a - b) Final Substrate Surface Tension (dynes/cm)
Water	72.6	11.7	60.9
Tricresyl phosphate	40.7	16.0	24.7
Propylene carbonate	41.0	10.5	30.5
Diethyl phthalate	36.0	11.2	24.8
Bis(2-ethylhexyl)adipate	29.6	6.2	23.4
Hexadecane	27.6	2.9	24.7

It is interesting that at the same monolayer concentration the decrease in substrate surface tension is not necessarily greatest for substrate liquids with the highest surface tension, and the same minimum surface tension is not observed with all substrates. This behavior indicates that the forces of attraction between the substrates and the polydimethylsiloxanes will vary from substrate to substrate. The 60.9-dyne/cm surface tension for water at 3 Å^2 per monomer is relatively high, indicating a high interfacial tension with polydimethylsiloxanes and thus a relatively low force of attraction. The organic liquids are apparently capable of a much greater degree of association with the polydimethylsiloxanes, as indicated by their greater mutual solubilities and thus lower interfacial tensions. Of the organic liquids, propylene carbonate, the most polar, was the only liquid to have a surface tension greater than 30 dynes/cm at 3 Å per monomer, at least 5 dynes/cm higher than the others.

DISCUSSION

It is apparent from a comparison of the F-vs-A curves of the polydimethylsiloxanes on all substrates that the molecular arrangement of the polymer molecules on certain organic liquids can be quite different from that on water, and in fact their orientation appears to vary with the nature of the organic liquid. To understand the behavior of polydimethylsiloxane films on organic liquids, it is well to begin by reviewing their behavior on water, which has been satisfactorily explained in terms of changes in molecular orientation with the state of compression (5,6,10,11,13).

At high areas per molecule the polymer chains are believed to be elongated at the water interface, the Si-O-Si bonds oriented toward the substrate with the methyl groups predominantly on the side of the chain away from the water. As the molecules in the surface are compressed, weakly associated water molecules in the film will be displaced, until at about 20 $Å^2$ per monomer the extended siloxane chains will begin fitting into a close-packed array. As the polymers are compressed below 20 $Å^2$ per monomer, the film pressure increases rapidly and the siloxane chains orient with the methyl groups outermost and in closest packing. Since further compression is impossible while maintaining all Si-O-Si groups in contact with water, subsequent decreases in area lead to one siloxane after another lifting off the surface and coiling into a series of spirals, averaging six siloxane units per spiral. This portion of the F-vs-A curve is characterized by a plateau at about 8.0 to 8.5 dynes/cm. At approximately 7 or 8 $Å^2$ per monomer the water surface is covered with a series of closely packed helices; further compression will cause the helices to be lifted from the surface, eventually collapsing.

In Fig. 2 many similarities are noted between the F-vs-A isotherms of the high-molecular-weight polydimethylsiloxanes on water and propylene carbonate. Extrapolation of the linear portions of the F-vs-A curves of these polymers on both propylene carbonate and water gave approximately the same limiting area per monomer, between 20 and 21 $Å^2$. In other words, on both propylene carbonate and water, polydimethylsiloxane molecules are probably fully extended on the substrate surface at high areas per monomer and begin to show a rapid rise in film pressure at that area per monomer where the fully extended chains begin to be closely packed on the surface. The F-vs-A isotherms on propylene carbonate begin to flatten out at 12 to 14 $Å^2$ per monomer, that point at which the siloxane molecules on water go into the helical configuration. There is no possibility of hydrogen bonding between propylene carbonate and the Si-O-Si groups, but the inference is that dipole-dipole attraction is sufficient to cause complete spreading of the molecules at high areas per molecule and that the monomers enter the helical configuration on compression, probably less ordered than on water.

The isotherms of F-vs-A per monomer for the higher-molecular-weight polydimehtylsiloxanes on tricresyl phosphate show the same changes in slope as on propylene carbonate but at much greater areas per monomer and at higher film pressures. The shape of these isotherms is also similar to that reported by Banks (7,9) for a polydimethylsiloxane on ethylene glycol. It is reasonable to assume, on the basis of the high polarity of the tricresyl phosphate, that the changes in orientation are similar to those found on water and propylene carbonate. Ellison and Zisman (8) also suggested that on tricresyl phosphate a polydimethylsiloxane film would be fully extended at high areas, with the Si-O-Si groups oriented toward the substrate.

The expanded nature of the polydimethylsiloxane monolayers on tricresyl phosphate is best explained on the basis of mixed monolayer formation, where significant numbers of the polar substrate molecules are entrained in the monolayer in close association with the siloxane groups. Because of the polarity of the phosphate group, the large size of the molecules, and the high bulk viscosity, it is not surprising that very stable mixed films result. Approximately, the same behavior was noted on tricresyl phosphate for polydimethylsiloxanes of 207, 80.2, and 47.7 repeating units; however, the degree of expansion of the polymer monolayer decreased with decreasing polymer chain length, indicating that the amount of solvent associated in the surface film is a function of polydimethylsiloxane molecular weight.

The higher-molecular-weight polydimethylsiloxanes on the less polar organic liquids, diethylphthalate and bis(2-ethylhexyl)adipate, gave isotherms significantly different from

those on propylene carbonate and tricresyl phosphate. They did not show the initial rapid rise in film pressure at about 20 $Å^2$ per monomer; they also did not show a decreasing slope after about 14 $Å^2$ per monomer. The first notable increase in film pressure occurred at 14 to 16 $Å^2$ per monomer, after which the film pressure increased monotonically. Extrapolation of the approximately linear portion of the curves of F vs A per monomer for the x = 207 polydimethylsiloxane on diethylphthalate and bis(2-ethylhexyl)adipate gave intercepts of 14 to 15 $Å^2$ per monomer, which correspond to the area that would be occupied by closely packed films of six-membered siloxane helices. This suggests that the polydimethylsiloxanes remained in the coiled configuration on the less polar substrates, even at large areas per molecule as suggested by Noll and coworkers (10,13). They concluded that on certain nonhydrogen-bonding liquids (including paraffin oils and polyglycol ethers), the attraction of the substrate for the polydimethylsiloxanes would not be sufficient to cause complete spreading of the film; rather the siloxanes would remain in the lower energy helix form even at the largest areas per molecule. They also concluded that no change in orientation of the molecules would occur over the entire range of pressure; that is, they remain in a helical configuration.

In the present investigation the behavior of the polydimethylsiloxane monolayers on hexadecane is similar to that on diethylphthalate and bis(2-ethylhexyl)adipate; that is, they seem to remain in a coiled, helical configuration regardless of the degree of expansion. As the polydimethylsiloxane molecular weight decreased, however, the monolayer solubility in hexadecane increased, until with 23.7 repeating units the film disappeared rapidly, showing relatively little increase in film pressure with film compression. The polydimethylsiloxane polymers on diethylphthalate and bis(2-ethylhexyl)adipate showed similar solubility behavior. As molecular weight decreased, the film stability decreased and solubility increased. In each case, in spite of the solubility, the shape of the curve was the same, the curve simply being displaced to lower areas per monomer. There was no indication of a change in orientation of the dimethylsiloxane polymers on these substrates as the chain length decreased.

The curves of F-vs-A per monomer on tricresyl phosphate and propylene carbonate showed significant changes in shape with the polymers of lower chain length. The siloxane polymer with an average of 23.7 repeating units per molecule still showed a limiting area per monomer of 20 to 22 $Å^2$ on propylene carbonate and tricresyl phosphate, indicating the molecules probably remained in the fully extended configuration at high areas per molecule. When the chain length was reduced to 10 or 14 repeating monomer units, the limiting areas on these substrates fell below 20 $Å^2$/monomer and the shape of the curves changed, no longer showing a decrease in slope at high film pressures. With fewer repeating Si-O-Si groups per molecule, and with the trimethyl end groups becoming a more significant portion of the molecule, the nature of the interaction between the siloxane polymers and the substrates changed. Apparently the polydimethylsiloxanes were no longer fully extended at low film pressures but remained in some type of helical configuration.

CONCLUSIONS

The present investigation showed conclusively that polydimethylsiloxanes can be studied as insoluble monolayers on a variety of organic liquids and that in many instances the films are extremely stable, are reversible, and can give film pressures as high or higher than normally found with polydimethylsiloxanes at the same area per monomer on water. In most instances the minimum surface tension of the substrate organic liquids was not much above that of the pure liquid polydimethylsiloxane as the area per monomer approached zero. In other words, there was no well-defined collapse pressure analogous to the equilibrium spreading pressure. This low surface tension indicates complete coverage of the surface by the polydimethylsiloxane film.

The stability of the polydimethylsiloxane monolayers appeared to depend on their solubility in the substrate, which is a function of the polymer molecular weight and their compatibility with the organic liquid. Generally, solubility increased with decreasing polymer molecular weight and with the decreasing polarity of the substrate.

The differences in behavior between the polydimethylsiloxane monolayers adsorbed on polar and nonpolar substrates is clearly reflected in their respective F-vs-A curves. On propylene carbonate and tricresyl phosphate, where it is suggested that the siloxane polymer chains of the higher-molecular-weight polymers are adsorbed in a fully extended configuration at large areas per molecule, the F-vs-A curves showed many similarities with the F-vs-A curves on water. On compression, the polydimethylsiloxane films on these substrates apparently assume a helical configuration, again much like the same compound on water. As the siloxane polymer chain length decreased, a point was reached where the orientation of the polymers on these polar organic solvents apparently changed. The F-vs-A curves indicated the shorter polymer chains were not fully extended but assumed a random coiled configuration, perhaps with the coils lying flat on the surface initially and then being forced into a vertical position upon compression. The low observed surface tensions indicate that on close packing, the surface is effectively covered with a close-packed film of $-CH_3$ groups.

On the nonpolar substrates the polydimethylsiloxane molecules did not appear to be fully extended even at large areas per molecule; they remained coiled in helices with six members per spiral, regardless of the state of compression. This brought primarily $-CH_3$ groups into contact with the substrate, the polar Si-O-Si groups all being oriented towards the center of the helix.

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13. ABSTRACT

A homologous series of polydimethylsiloxanes was spread as insoluble monomolecular films on water and on a number of organic liquids of varying surface tension and surface composition. The organic liquids studied as substrates were tricresyl phosphate, propylene carbonate, diethylphthalate, bis(2-ethylhexyl)adipate, and hexadecane. Monolayer stability and insolubility were found to vary with the molecular weight of the polydimethylsiloxane and the polarity of the substrate liquid. Stable, reversible monomelecular films were formed on all substrates by the higher-molecular-weight polymers (mol wt >6000); however, film stability decreased with decreasing polymer molecular weight and decreasing substrate polarity.

The orientation of the polydimethylsiloxane films at the organic liquid/air interfaces depended on the surface composition of the substrate liquids. On tricresyl phosphate and propylene carbonate the high-molecular-weight polymers adsorbed in a fully extended configuration at large areas per molecule, analogous to their behavior on water. With compression they assumed a helical configuration with six monomer units per helix. On the less polar substrates the polydimethylsiloxanes apparently remained in the helical configuration regardless of the state of compression.

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