Properties of Poly[methyl(*n*-alkyl)siloxane] and Poly[methyl(3,3,3-trifluoropropyl)siloxane] Monolayers Adsorbed on Water

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ABSTRACT: Relationships of film pressure (F) *vs.* area (A), surface potential (ΔV) *vs.* A, and the vertical component of the surface dipole moment (μ_p) *vs.* A were studied of two groups of liquid polysiloxanes, $(CH_3)_3Si[OSi(CH_3)(R)]_nOSi(CH_3)_3$, spread on water as adsorbed monolayers. In the first group R is either CH_3, C_2H_5, or n-C_4H_9 and n is 14 or 12; in the second group R is $(CH_2)_2CF_3$, and n varies as the 25° viscosities of the polymers range from 72 to 1000 cSt. For any given area in the first group, the three surface-physical properties measured decreased in value as the carbon number increased. The F *vs.* A isotherms of the second group of polymers are similar to one another but are different from the members of the first group. The electrical properties (ΔV *vs.* A and μ_p *vs.* A) show that the net dipole moment per monomer of the $(CH_2)_2CF_3$ substituted polysiloxanes is oriented with the negative end away from the water, *i.e.*, in the opposite direction from that of the n-alkyl substituted polymers. It was possible to compute, under a given set of conditions, μ_p of the terminal CF_3 group only, and the values are in good agreement with those found by us in an earlier investigation of progressively fluorinated n-alkanoic carboxylic acids adsorbed closely packed on water. All results are discussed in terms of chain length and fluorine subsitution for hydrogen in the alkyl side chains, tactic configuration, effects of steric hindrances of the substituents, and possible molecular arrangements of the various adsorbed polymer chains. It is concluded that the difference in magnitude and sign of μ_p per close-packed, well-oriented monomer is highly indicative of a major difference in the biochemical and medical properties of these two classes of poly(organosiloxanes).

Of the numerous types of linear poly(organosiloxanes) synthesized in the past 35 years, the surface-chemical properties of the poly(dimethylsiloxanes), the poly(diethylsiloxanes), and the poly[methyl(phenyl)siloxanes] were the first to be investigated extensively as monolayers adsorbed on water.[1-7] Later investigations reported on the spreading behavior of these polymers on the surfaces of organic liquids.[8-10] In the past decade much attention has been given the poly[methyl(alkyl)siloxanes] and the poly[methyl(3,3,3-trifluoropropyl)siloxanes] as the result of the attempts to improve the boundary lubricating properties of the poly(organosiloxanes), especially through the work of Brown,[11] Pierce,[12] and Schiefer and Van Dyke.[13] Recently, the film pressure (F) *vs.* area per adsorbed molecule (A) on water surfaces has been reported for the latter two classes of poly(organosiloxane) polymers by Noll, Steinbach, and Sucker.[14]

We also have investigated the F *vs.* A properties, as well as the surface electrostatic potential differences (ΔV) *vs.* A. Here ΔV is measured between an electrode in the air above the film adsorbed on water and an electrode submerged under the water; in this way, we have been able to calculate the perpendicular component (μ_p) of the apparent dipole moment (μ) per molecule or per monomer of each type of poly(organosiloxane). Our results will exemplify why it is generally advantageous in surface-chemical investigations to follow simultaneously the changes in more than one surface property of the adsorbed film. Many earlier examples of this point will be found in Adam's classic review.[15]

The purpose of this report is to summarize our F *vs.* A and ΔV *vs.* A results on some recently available poly(organosiloxanes) and to discuss the dipole moment per molecule (or per monomer) as a function of film pressure as the principal subject of interest. Finally, we will compare the resulting electrostatic dipole properties of the methyl(n-alkyl)siloxane and of the methyl(3,3,3-trifluoropropyl)siloxane monomers in relation to that of the dimethylsiloxane monomer.[1,2]

Experimental Section

The pure open-chain, trimethylsilyl end-blocked poly(dimethylsiloxane) tetradecamer used in this investigation was a gift of the Union Carbide Co.; the trimethylsilyl end-blocked poly[methyl(n-alkyl)siloxane] dodecamers,[11] where the n-alkyl represented either the ethyl or butyl group, were obtained through the cooperation of the Research Laboratory of the General Electric Co.; and the trimethylsilyl end-blocked poly[methyl(3,3,3-trifluoropropyl)siloxanes][12] were obtained from the Dow Corning Co. in viscosity grades at 25° of 72, 130, 300, and 1000 cSt. The three

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(1) H. W. Fox, P. Taylor, and W. A. Zisman, *Ind. Eng. Chem.*, **39**, 1401 (1947).

(2) H. W. Fox, E. M. Solomon, and W. A. Zisman, *J. Phys. Colloid Chem.*, **54**, 723 (1950).

(3) M. J. Newing, *Trans. Faraday Soc.*, **46**, 755 (1950).

(4) W. Noll, H. Steinbach, and C. Sucker, *Ber. Bunsenges. Phys. Chem.*, **67**, 407 (1963).

(5) W. Noll, H. Steinbach, and C. Sucker, *Kolloid-Z. Z.-Polym.*, **204**, 94 (1965).

(6) W. D. Garrett and W. A. Zisman, *J. Phys. Chem.*, **74**, 1796 (1970).

(7) N. L. Jarvis, *ibid.*, **70**, 2037 (1966).

(8) W. H. Banks, *Nature (London)* **174**, 365 (1954).

(9) A. H. Ellison and W. A. Zisman, *J. Phys. Chem.*, **60**, 416 (1956).

(10) N. L. Jarvis, *J. Colloid Interface Sci.*, **29**, 647 (1969).

(11) E. D. Brown, Jr., *ASLE Trans.*, **9**, 31 (1966).

(12) O. R. Pierce, *Prepr., Amer. Chem. Soc., Div. Org. Coatings Plast.*, **29** (2), 373 (1969).

(13) H. M. Schiefer and J. Van Dyke, *ASLE Trans.*, **7**, 32 (1964).

(14) W. Noll, H. Steinbach, and C. Sucker, *Kolloid-Z. Z. Polym.*, **236**, 1 (1970).

(15) N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd ed, Oxford University Press, London, 1941.

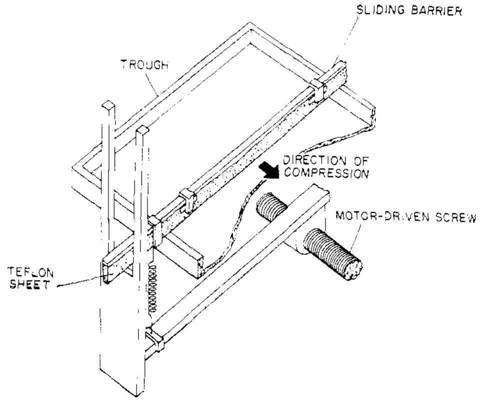

Figure 1. Schematic of sliding barrier arrangement.

poly[methyl(*n*-alkyl)siloxanes] were each percolated through a column of activated Florisil in order to remove any more surface-active impurities; since the higher viscosities of the poly[methyl(3,3,3-trifluoropropyl)siloxanes] prevented the liquids from passing readily through a long adsorption column, these compounds were used as received.

Solutions of each polymer were prepared in concentrations of from 1×10^{18} to 4×10^{18} monomers/ml of spreading solvent. The spreading solvent used was either *n*-hexane (pure grade) from Phillips Petroleum Co. or Freon TF ($CCl_2F-CClF_2$, bp 47.6°) from E. I. du Pont de Nemours and Co. Before use each solvent was purified by being freshly passed through an adsorption column containing a layer of activated Florisil followed by one of alumina. The poly[methyl(*n*-alkyl)siloxane] solutions were prepared in either solvent, but Freon TF proved to be preferable for the poly[methyl(3,3,3-trifluoropropyl)siloxanes] because of their low solubilities in hexane. Since the F *vs.* A isotherms for monolayers spread on clean water surfaces were identical for a given poly(organosiloxane) with either solvent, only the results obtained with Freon TF spreading solvent are reported here in order to maintain comparable experimental conditions. Each polymer solution was delivered dropwise to the clean water surface with a calibrated self-adjusting micropipet, and the behavior of the resulting adsorbed monolayer was then investigated.

The film balance consisted of a Teflon-coated aluminum trough, 60 cm × 14.0 cm in area and 1.5 cm deep. To avoid leakage of the monolayer, an 0.1-mm thick Teflon sheet was clamped tightly around the Pyrex sliding barrier which, in turn, was secured by springs to a metal bar running below the width of the trough (Figure 1). The bar was coupled with a variable-speed motor drive to permit continuous compression or expansion. The permissible rate of compression was determined by preliminary measurements of the time necessary for the film pressure to remain constant on discontinuation of compression. The optimum rate thus ascertained was 0.33 cm/min for all compounds reported here.

Changes in film pressure were measured by means of a platinum Wilhelmy plate and were recorded by the electric strain gauge method recently described by Jarvis.[10] The Wilhelmy plate was 3.95 cm long, 1.0 cm high, and 0.0005 cm thick, and its surface was roughened with a 400A grit silicone carbide paper to make the apparent contact angle zero. The plate was attached to a Statham UC2 strain gauge and a UR5 transducer readout. The signal was recorded continuously on a double-channel Varian G-22 recorder with Type B-22 input chassis; the recorder sensitivity could be adjusted so that each division on the chart paper corresponded to a difference in film pressure of 0.10 dyn/cm.

Surface potential measurements were made with a commercial Am^{241} electrode made of a flat sheet of brass 5 cm × 5 cm which had been covered with gold foil. The electrode was shielded from extraneous electrostatic effects by a grounded copper wire screen cage placed around it and was connected to a Keithley 610 electrometer *via* an Amphenol RG shielded cable. A clean platinum electrode dipped into the aqueous substrate provided the ground return. The resulting surface potential signal was recorded continuously on the Varian G-22 recorder, with a sensitivity of 10 mV/division of the chart paper. The film balance, strain gauge, and americium electrode were enclosed in a Lucite box to maintain a dust-free, high-humidity atmosphere. All experiments were carried out in a constant-temperature room controlled at 22 ± 0.2°.

Before every change to a new spreading solution and after from three to five independent runs, the film trough was thoroughly washed with a Tide solution, copiously rinsed with running tap water, and finally washed with distilled water, until it was so uniformly hydrophobic that all the water rolled off the surface leaving it completely dry. The water used as substrate was passed once through a tin-lined Stokes still and then twice through an all-quartz still; it had a conductivity of 1×10^{-6} ohm^{-1} and a pH of 5.8 when in equilibrium at 22° with atmospheric carbon dioxide. After the substrate was swept clean with the Teflon-coated barriers, the Wilhelmy plate was cleaned just before immersion by heating it to a dull red heat and then lowered until it just touched the surface; the americium electrode was lowered to a distance of from 2 to 3 mm parallel to and above the water surface. Because of the large area of the electrode, an appreciable variation of distance from the surface was permissible without affecting the results. The recorder pens were then adjusted to zero readings for the film pressure and surface potential.

After several minutes the spreading solution was added dropwise over the length of the clean water-covered area of the trough and then allowed to equilibrate for approximately 15 min before the onset of film compression. Changes in F and ΔV were recorded as functions of A. The stability of the monolayer was determined by interrupting the preliminary run at various film pressures and checking for any decrease in F with time; this was also repeated at the end of each run at the highest attained value of F. Film stability was also determined by comparing plots of the F *vs.* A and ΔV *vs.* A data obtained on film compression with results observed on film expansion and noting the amount of hysteresis, if any. The contact angle of the substrate on the platinum plate appeared to remain zero during the entire course of each run. At the completion of the run, the Wilhelmy plate and the electrode were raised from the surface, the adsorbed film was swept away from the trough with the barriers by overflowing it over the edge for several times, additional water was added, and a new run was begun.

Five or more such runs with each compound were made with at least two different volumes of solution delivered to the surface. Unless indicated otherwise, the reproducibility of measurements was never more than ±0.2 dyn/cm for F and ±0.03 V for ΔV.

Results and Discussion

Force *vs.* Area Isotherms. In Figure 2 are given the F *vs.* A curves (where A is the area per molecule) for the poly[methyl(*n*-alkyl)siloxanes] of the general formula $(CH_3)_3Si[OSi(CH_3)R]_nOSi(CH_3)_3$, where R is CH_3, C_2H_5, or C_4H_9. Where R is CH_3, $n = 14$; where R is C_2H_5 or C_4H_9, $n = 12$. However, since no appreciable difference in the isotherms could be detected with such minor variations in the length of the principal molec-

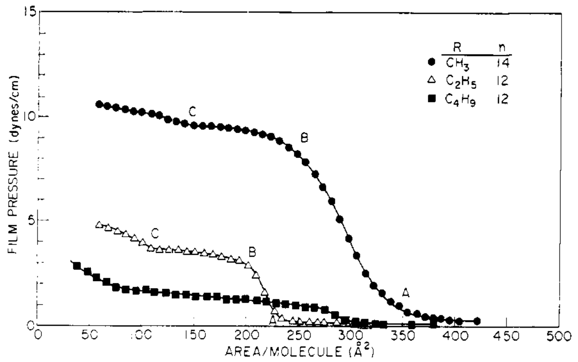

Figure 2. Film pressure *vs.* area per molecule isotherms of $(CH_3)_3Si[OSi(CH_3)(R)]_nOSi(CH_3)_3$.

ular chain, the results obtained could be compared directly. No loss in pressure with any compound was observed when compression was interrupted during the run or when the film was permitted to remain on the surface at the highest pressure; furthermore, the curve for each compound was reversible over the whole pressure range. The points on each curve represent a single run taken from the recorder tracing. The *F vs. A* curves are in good agreement with the results obtained by Noll and coworkers[14] as well as those of Jarvis.[16]

The data from Figure 2 were then recalculated in order to express *A* as the area per monomer by multiplying the weight in grams of the polymer spread on the water by Avogadro's number (6.025×10^{23}), and then dividing by the gram molecular weight of the monomer unit to obtain the number of monomers (*n*) available. The area per monomer could then be computed by dividing the respective area by *n*.

The *F vs. A* curve (Figure 3a) of the poly(dimethylsiloxane) thus obtained was in excellent agreement with various past reported determinations.[1–7,10,14,16–18] Regions marked A, B, and C in Figures 2 and 3a, where conformational changes of such polymers had been established in earlier investigations and were confirmed recently in ref 6, were again evident, and these regions appeared at the same areas per molecule (or per monomer), respectively. Briefly, the polymer chains extended at high areas per molecule become, on compression, condensed into a close-packed array in region A. Between regions A and B the SiO bonds lift out of the water, the polymer molecule buckles and in region B begins to coil into a series of helices until in region C the molecule becomes compressed into an arrangement where the axis of the helix is oriented horizontally. On further compression, the helices are lifted from the surface if *n* is not too great, or collapse into a polymolecular film if *n* is large.[6,7]

The *F vs. A* isotherms for the *n*-alkyl-substituted siloxanes assumed a different profile on film compression (Figures 2, 3b, and 3c). The curve for the polymer having R = C_2H_5 was displaced toward much smaller areas per molecule and much lower film pressure, although three transformation regions reminiscent of regions A, B, and C of the poly(dimethylsiloxanes) were still noticeable. The curve for the polymer having R = C_4H_9 rose less steeply; only slight indications were seen of regions analogous to A, B, and C. Other investigators[14,16] have obtained very similar *F vs. A* isotherms in agreement with those reported in Figure 2. There are various factors contributing here which need to be considered to explain these observations. First, increasing steric hindrance is created as the side chain R becomes longer. Second, the presence of various

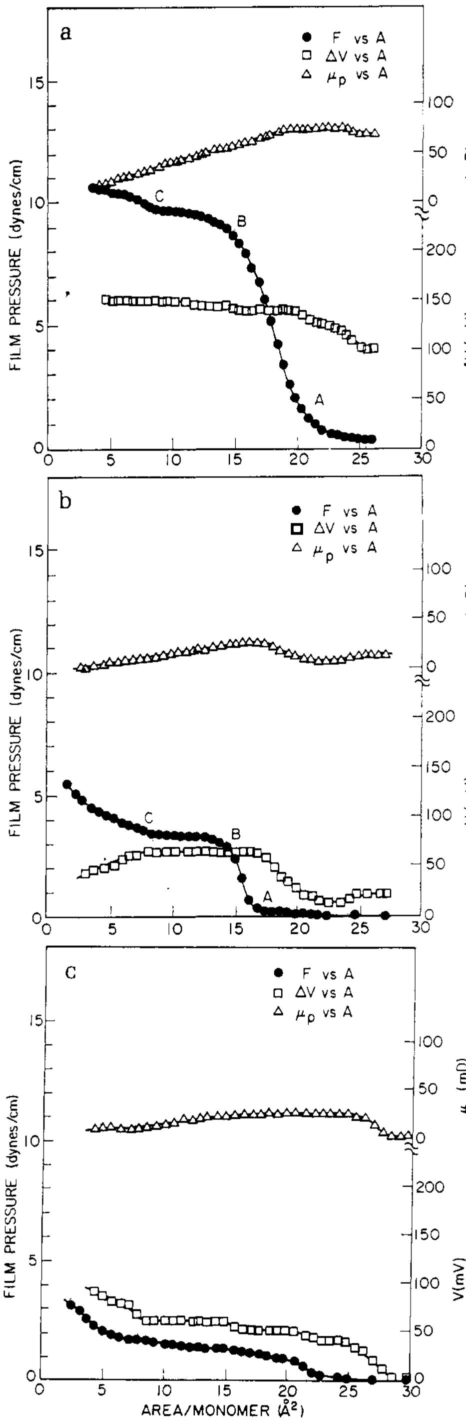

Figure 3. Properties of monolayers of (a) $(CH_3)_3Si[OSi(CH_3)_2]_{14}OSi(CH_3)_3$, (b) $(CH_3)_3Si[OSi(CH_3)(C_2H_5)]_{12}OSi(CH_3)_3$, (c) $(CH_3)_3Si[OSi(CH_3)(C_4H_9)]_{12}OSi(CH_3)_3$.

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(16) N. L. Jarvis, to be published.

(17) A. A. Trapeznikov, I. I. Latsepina, T. A. Gracheva, R. N. Shcherbakova, and V. A. Ogarev, *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **160**, 174 (1965).

(18) W. Noll, *Kolloid-Z. Z. Polym.*, **211**, 98 (1966).

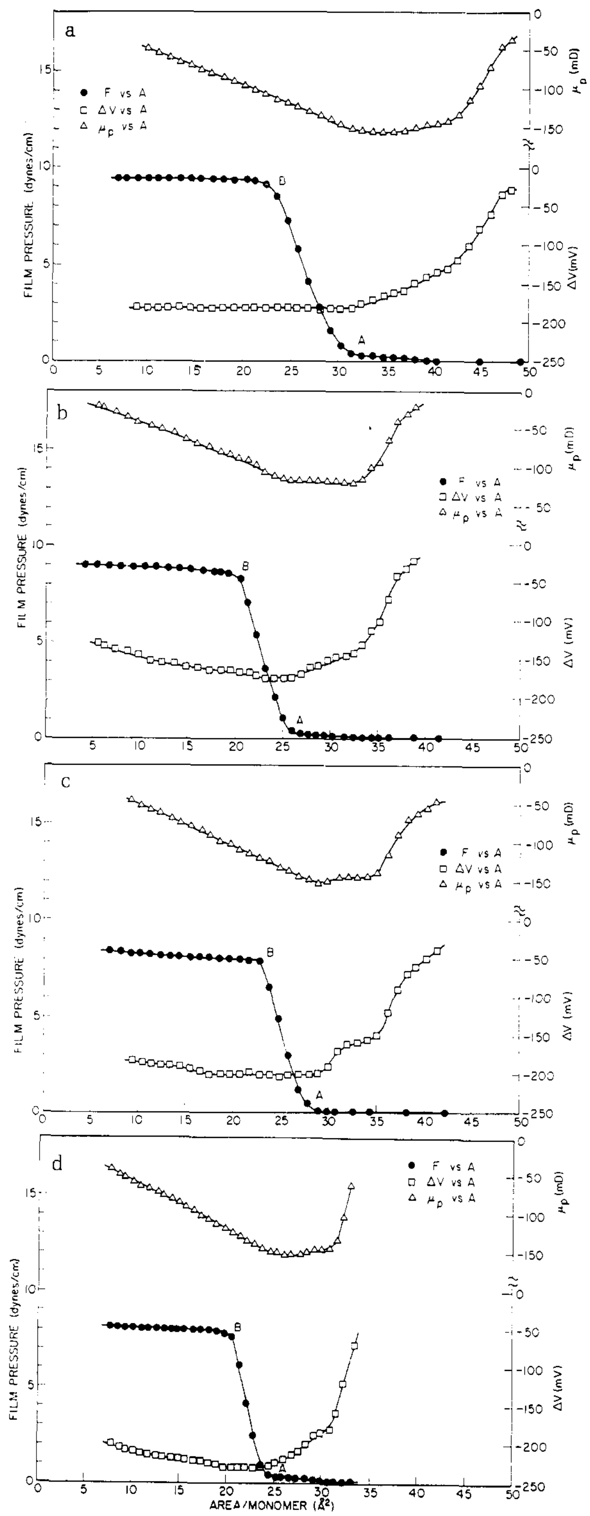

Figure 4. Properties of monolayers of $(CH_3)_3Si[OSi(CH_3)(C_2H_4CF_3)]_nOSi(CH_3)_3$ with 25° viscosities of (a) 72 cSt, (b) 130 cSt, (c) 300 cSt, (d) 1000 cSt.

possible tactic configurations of the polymer, caused by an asymmetry of the monomer unit, leads to differences in the packing and orientation of the substituents and dictates the preferred state of relaxation, extension, or coiling of the polymer chains. An increase in the carbon number of the R substituent leads to a decrease of the spreading ability on water as the outermost constitution of the molecule makes it act more like a paraffin. In an early study, Fox, Solomon, and Zisman[2] reported that an increase in the hydrogen ion concentration in the water substrate caused a more completely horizontal orientation of the poly(dimethylsiloxanes) at lower film pressures; at values of pH below 3 or above 9, the hydrated polymer hydrolyzed until completely depolymerized. Noll and coworkers[14] have recently reported that the *n*-alkyl-substituted poly(organosiloxanes), when spread on water at low film pressures, are partially oriented in helical and condensed configurations and are only forced into an extended chain by a high hydrogen ion concentration of the water.

The volume of an $SiO(CH_3)(C_2H_5)$ monomeric unit is 120 Å³ when computed from the average area of 20 Å² and height of 6 Å obtained from measurements on the various tactic configurations formed with Stuart–Briegleb molecular models. Including the contribution for both trimethylsilyl end groups, the molecular volume of the extended polymer chain containing 12 monomers then should be 1692 Å³. An average molecular height of 7.3 Å was calculated at A_0, the limiting area per molecule (or per monomer), where the polymer chain was fully extended and at its most condensed state before buckling. A_0 is 230 Å² in Figure 2 and 16.6 Å² in Figure 3b. The value of 7.3 Å is somewhat greater than the value of 6 Å estimated from the molecular model and may indicate that the principal molecular chains are not fully extended. It is generally recognized that open chain poly(dimethylsiloxanes) assume a helical shape in their liquid state and straighten out when pressure or other forces are applied.[19,20] The act of spreading such polymers upon the clean surface of water is sufficient to uncoil completely the sterically unhindered molecular chain because of the hydrogen-bonding ability of the SiO linkage;[1] this result, however, becomes progressively more difficult to attain with side chains longer than methyl because of increased steric hindrance and tactic configurations.

Region C was not too well defined for the poly[methyl(ethyl)siloxane], but was indicated to occur (Figure 2) at an area per molecule of about 110 Å². The calculated thickness for such an area is 15.7 Å, somewhat larger than the measured height of 12.0 Å for the tightly coiled helix from molecular ball models made of six monomer units per turn, indicating a less-ordered helix formation. The transformation points on the *n*-butyl-substituted siloxane *F vs. A* isotherms were so indistinct that no definite conclusions could be made about the corresponding molecular reorientation.

In Figure 4 are shown the *F vs.* area per monomer curves obtained from $(CH_3)_3Si[OSi(CH_3)(C_2H_4CF_3)]_n$-$OSi(CH_3)_3$ polymers of four different viscosities. No data are available from the producer of the average molecular weights or of the molecular weight distribution curves of these liquids; however, these polymers are reported to be composed of a mixture of homologs. An order of magnitude could be deduced by comparison with the compound studied by Noll, *et al.*,[14] where *n* was 10 and the viscosity at 20°

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(19) M. J. Newing, *Trans. Faraday Soc.*, **46**, 613 (1950).

(20) E. L. Warrick, M. J. Hunter, and A. J. Barry, *Ind. Eng. Chem.*, **44**, 2196 (1952).

TABLE I
MONOLAYER PROPERTIES OF $(CH_3)_3Si[OSi(CH_3)(R)]_nOSi(CH_3)_3$

	Area/monomer, Å^2			F, dyn/cm			ΔV, mV			μ_p, mD		
R	A	B	A_0	A	B	7Å^2	A	B	7Å^2	A	B	7Å^2
CH_3 (n = 14)	22	14	21.0	0.7	9.1	10.2	125	145	150	75	50	30
C_2H_5 (n = 12)	17	14	16.6	0.4	3.1	3.7	60	65	60	25	22	15
C_4H_9 (n = 12)						2.7			75			15
$C_2H_4CF_3$ (72 cSt)	31	22	30.0	0.3	9.2	9.4	−175	−175	−175	−155	−110	−40
$C_2H_4CF_3$ (130 cSt)	26	19	25.6	0.3	8.4	9.0	−170	−170	−140	−120	−90	−25
$C_2H_4CF_3$ (300 cSt)	29	23	27.4	0.1	7.9	8.4	−200	−200	−190	−150	−120	−40
$C_2H_4CF_3$ (1000 cSt)	24.5	20	24.0	0.4	7.8	8.2	−230	−230	−200	−150	−125	−40

was 165 cSt. That would put the average of w for two of our polysiloxanes at below 10 and the remaining two compounds at above 10. No decrease in F was observed at any pressure when compression was interrupted, nor was there any appreciable hysteresis between the compression and expansion curves; the largest amount of hysteresis, 0.5 dyn/cm, was observed on the polymer having a viscosity of 72 cSt.

One would expect the F *vs.* A isotherms of the poly[methyl(3,3,3-trifluoropropyl)siloxanes] to fall between the isotherms of the poly[methyl(ethyl)siloxanes] and the poly[methyl(*n*-butyl)siloxane]. However, the general profile of the isotherm for the fluorinated siloxanes resembled that the of poly(dimethylsiloxanes), missing only region C. This is in excellent agreement with the recent results of Noll, Steinbach, and Sucker.[14] There were differences, however, in the individual curves as regards the onset of film pressure (region A) with respect to the area per monomer (Table I) and the value of the plateau film pressure. When the linear portions of the rapidly rising portion of the F *vs.* A isotherms were extrapolated, there resulted limiting areas/monomer (A_0) of 30.0, 25.6, 27.4, and 24.0 Å^2, respectively, for the polymers with increasing viscosity (Table I). Values of F for these monolayers at A = 7 Å^2 (about the limit of our observations) were 9.4, 9.0, 8.4, and 8.2 dyn/cm (Table I). Essentially, our F *vs.* A graphs at high values of F and low values of A (as an example, when $A < 15$ Å^2 in Figure 4d) suggest strongly that the limiting value of F is the equilibrium spreading pressure (F_e). A typical collapse curve, as observed on compounds such as pure oleic acid, usually remains constant with decreasing A.[21] The curves in Figures 4b, 4c, and 4d do not level off to a horizontal plateau, but continue to rise very slightly. The cause is believed to be the mixture of various values of n in each polymer resulting in an average value of F_e. From the shape of the plateau region in these instances and, in general, because of the steric hindrance to adlineation, we can conjecture that helices are formed only imperfectly and on further compression become disoriented, slip over one another, and finally collapse.

Previous studies on poly(dimethylsiloxanes)[1,10,14] had shown that with increasing molecular weight there was a slight trend to decreasing area/monomer for the onset of noticeable film pressure (region A) and also to decreasing plateau film pressures. This had suggested that increasing steric hindrance prevents the long-chain polymer molecules from being fully extended. In the case of the poly[methyl(3,3,3-trifluoropropyl)siloxanes], consideration has to be given to the additional steric hindrance by the large 3,3,3-trifluoropropyl substituent and the asymmetry of the monomer unit. Since each polymer is probably composed of a combination of all tactic configurations and in random order, full extension of the high molecular polymer chains becomes further inhibited when compared to the more symmetric poly(dimethylsiloxanes), and this then accounts for the area per monomer decrease with increasing molecular weight in regions A and B and in the value of A_0. We have no explanation for the reversal in the order of values of A for the polymers having viscosities of 130 and 300 cSt; we suggest a preponderance of a particular tactic and/or steric configuration or a larger variation of molecular weights and chain lengths in either one of them.

If we use the same approach in measuring the areas per monomer from molecular ball models to calculate the thickness for the extended chain, we obtain an average measured value of 6.4 Å for all tactic configurations and average calculated values of 5.9, 7.3, 6.5, and 7.4 Å at A_0 for the four polymers of increasing viscosity, respectively. Since in these calculations the contribution of the end groups had to be neglected, the most representative values of the areas per monomer are probably for the polymer having the highest viscosity, where the principal chain length is sufficiently long to permit this neglect.

Electrical Properties. The contact potential difference ΔV caused by the adsorption of a monolayer of polar–nonpolar molecules on an aqueous substrate results because each such molecule contains one or more oriented electrostatic dipoles. Similarly, a monolayer of polymeric molecules adsorbed on an aqueous substrate is composed of numerous monomers, each of which may contain one or more oriented electrostatic dipoles. The classic Helmholtz equation, $\Delta V = 4\pi n \mu_p$, can be applied to calculate ΔV, the difference in the electrostatic surface potential between the clean water surface and the surface covered by the adsorbed monolayer; here μ_p is the perpendicular component of the total electrostatic dipole moment per adsorbed monomer, and n is the number of monomers adsorbed per unit area. When a poly(organosiloxane) is adsorbed in close packing on the surface of the water and there is a substituted n-alkyl hydrocarbon group attached to each silicon atom, as in a poly(dialkylsiloxane), the associated dipole contribution is directed so that its positive end is pointed away from the water surface.

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[21] E. K. Rideal, "An Introduction to Surface Chemistry," 2nd ed, Oxford University Press, Cambridge, England, 1930, p 128.

It had been shown that close-packed, terminally halogenated, aliphatic carboxylic acids adsorb on water with the large dipole arising from the halogenated group pointed in the opposite direction.[22,23] Hence, we can recognize the possibility that ΔV and μ_p for an adsorbed dialkylsiloxane monomer, which has one 3,3,3-trifluoropropyl substituent on the silicon atom, could each have a net negative value.

Experimental results are shown in Figures 3 and 4 and in Table I for regions A and B and for an area per monomer of 7 Å^2. Values of ΔV found for the dimethylsiloxane monomer approximate closely the early results reported by Fox, Taylor, and Zisman.[1] This monomer, as well as the methyl(ethyl)siloxane monomer, approached its highest value of ΔV at the plateau region of the F *vs.* A curve where helix formation and the subsequent coil compression occurred, whereas the poly[methyl(butyl)siloxane] monomer showed continued increase in ΔV with decrease in area. With increase in the number of carbon atoms in R, there was a decrease in ΔV for any one given area per monomer. Negative values of ΔV were obtained only with the poly[methyl(3,3,3-trifluoropropyl)siloxanes], the most negative occurring between regions A and B for each such polymer. To the left of region B, no significant change in ΔV with decreasing area per monomer was observed for the compound with the lowest viscosity (72 cSt), whereas ΔV values of the more viscous polymers became gradually (and slightly) less negative. This may indicate that, while the long-chain molecules of the latter curled on compression into helices, the short moleculer chains of the former could only lift off the surface and remained tilted at an acute angle to the substrate.

Figures 3 and 4, and Table I, also give the values of μ_p per monomer. The difference in sign indicates that whereas in the *n*-alkyl substituted monomers the negative end of μ_p is directed toward the water, in the 3,3,3-trifluoropropyl-substituted monomer the negative end of the dipole is directed away from the water. Values obtained had their maximum absolute values at monomeric areas larger and up to that observed in region A; at higher compression, μ_p slowly and linearly approached zero with decreasing areas per monomer. Where μ_p was essentially constant, obviously no significant reorientation of the polymer molecule was taking place. On further compression below the value of A_0, there was an increase in slope which corresponded to the initial buckling of the monolayer; however, no further increase in slope was apparent for the subsequent configurational rearrangements of the polymer chains. This is in excellent agreement with the observations of Fox, Taylor, and Zisman[1] on poly(dimethylsiloxanes) and poly(diethylsiloxanes). It is noteworthy that linear portions of the μ_p *vs.* A isotherms were numerically identical for the poly[methyl(ethyl)siloxane] and the poly[methyl(*n*-butyl)siloxane] monomers. Regardless of the viscosity (or average molecular weight), the μ_p *vs.* A isotherms of the poly[methyl(3,3,3-trifluoropropyl)siloxanes] were either identical or were very close to one another.

The value of μ_p per monomer can be approximately treated as the vector resultant of the several contributing dipole components present in that monomer.[24] For a monomer adsorbed at the water–air interface these are (a) the contribution of the polar –SiO– group, (b) that of the $-CH_3$ group attached to the Si atom, (c) that of the other alkyl group attached to the Si atom, (d) that of the resultant arising from the reorientation of the water dipoles in the immediate vicinity of the adsorbed siloxane monomer, and (e) the contribution of any ionic double layer present just below the water–air interface. It will be assumed that contributions (d) and (e) do not alter the contributed moments of (b) and (c) because of either their greater distances from the water–air interface or the lower strength of the hydrogen bonds. Since it does not seem possible yet to separate the contribution of the hydrophilic polar –SiO– group from those of the adsorbed water layer polarized by it (d), and of the ionic double layer (e), the three terms (a), (d), and (e) have been lumped into a single term, $\mu_{p(SiO)}$. Therefore, μ_p for the dialkyl-substituted siloxane monomer can be expressed as

$$\mu_p = \mu_{p(SiO)} + \mu_{p(CH_3)} + \mu_{p(CH_2 \cdot \cdot CH_2CH_3)} \qquad (1)$$

where μ_p is the observed value, $\mu_{p(CH_3)}$ the contribution of the $-CH_3$ group, and $\mu_{p(CH_2 \cdot \cdot CH_2CH_3)}$ the contribution of the other *n*-alkyl group. The dipole moment of an ethyl group can be considered the same as those of higher alkyl groups, since additional $-CH_2-$ groups affect the moment little.[25] Even the difference in dipole contributions between an ethyl group and a methyl group, as determined from many compounds in the gaseous state (or in solution), is at most 0.2 D, but more often it is less than 0.1 D.[26] Therefore, the difference between the vertical components of μ_p for the alkyl substitutents is usually less than 0.1 D, which is negligible compared to the uncertainties in the reported values of $\mu_{(CH_3)}$.[27] Hence, assuming as a reasonable approximation that the dipole contribution of $\mu_{p(CH_2 \cdot \cdot (CH_2CH_3)}$ is the same as that of $\mu_{p(CH_3)}$, eq 1 becomes simply

$$\mu_p = \mu_{p(SiO)} + 2\mu_{p(CH_3)} \qquad (2)$$

When the adsorbed molecule has three fluorine atoms on the 3-carbon atom in the propyl chain, then

$$\mu_p = \mu_{p(SiO)} + \mu_{p(CH_3)} + \mu_{p(CF_3)} \qquad (3)$$

From the assumptions made, it follows that at any definite state of molecular orientation and packing of the poly(organosiloxane), $\mu_{p(SiO)}$ should be the same whether the *n*-alkyl substituent is terminally fluorinated or not. Such a state comparable for each compound is in region A, where the extended polymer is in closest packing just before buckling out of the water surface and where μ_p is at its maximum value. Although many

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[22] M. K. Bernett and W. A. Zisman, *J. Phys. Chem.*, **67**, 1534 (1963).

[23] M. K. Bernett, N. L. Jarvis, and W. A. Zisman, *ibid.*, **68**, 3520 (1964).

[24] J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York, N. Y., 1961, pp 70–74.

[25] C. P. Smyth, "Physical Methods of Organic Chemistry," A. Weissberger, Ed., 2nd ed, Vol. I, part II, Interscience, New York, N. Y., 1949, p 1614.

[26] L. G. Groves and S. Sugden, *J. Chem. Soc.*, 158 (1937).

[27] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, N. Y., 1955, pp 240–243.

TABLE II
ELECTRICAL PROPERTIES OF
$(CH_3)_3Si[OSi(CH_3)(R)]_nOSi(CH_3)_3$

R	$\mu_{p(\max)}$, D	$\mu_{p(\mathrm{SiO})}$, D (from eq 2)[a]	$\mu_{p(\mathrm{CH_3})}$, D (from eq 3)
CH_3	0.075	0.675	
$C_2H_4CF_3$ (72 cSt)	−0.155		−0.530
$C_2H_4CF_3$ (130 cSt)	−0.120		−0.495
$C_2H_4CF_3$ (300 cSt)	−0.150		−0.525
$C_2H_4CF_3$ (1000 cSt)	−0.150		−0.525

[a] Assuming $\mu_{p(\mathrm{CH_3})} = -0.300$ D.

uncertainties remain in the literature about the correct value of $\mu_{(\mathrm{CH_3})}$[27] a value of 0.4 D for the dipole moment of the terminal CH_3 group has been chosen by many investigators, with a polarity of C^+–H^-.[28,29] Thus, $\mu_{p(\mathrm{SiO})}$ can be calculated from eq 2 as 0.675 D for the dimethylsiloxane by using −0.3 D as $\mu_{p(\mathrm{CH_3})}$ (Table II, column 3). Equation 3 was then used to compute $\mu_{p(\mathrm{CF_3})}$ from $\mu_{p(\mathrm{SiO})}$ by assuming that the $\mu_{p(\mathrm{SiO})}$ values are the same for the fluorinated and the unfluorinated monomers. The results thus obtained range from −0.495 to −0.530 D and are listed in column 4, Table II, for each of the four poly[methyl(3,3,3 - trifluoropropyl)siloxanes]. These values are in excellent agreement with the values of −0.490 to −0.540 D (assuming a polarity C^+–H^-) reported by Bernett and Zisman[22] for μ_p of $F(CF_2)_m$ groups (where m ranged from 1 to 10), although in that study the $F(CF_2)_m$ groups were terminally attached to fatty acid segments, a totally different molecular structure from poly(organosiloxanes).

Conclusions

The behavior of well-defined poly[methyl(*n*-alkyl)-siloxanes] was observed when adsorbed on water as monolayers. As the *n*-alkyl substituent increased in carbon number, values of F, ΔV, and μ_p decreased for a given area per monomer because the polymer molecule approached a more paraffinlike character which decreased its spreading ability. When the *n*-alkyl substituent was replaced with a 3,3,3-trifluoropropyl group, some noteworthy changes in the F *vs.* A isotherms indicated that the conformational rearrangements of such polymers were not identical with those of the poly[methyl(*n*-alkyl)siloxanes]. We propose that the chains of the adsorbed poly[methyl(3,3,3-trifluoropropyl)-siloxanes] are prevented from coiling under lateral pressures to form perfect helices because of the various tactic configurations of the bulky substituent and the concomitant steric hindrance. Under high compressions, the imperfectly formed helices therefore become disoriented, slip over one another, and finally collapse.

The electrical properties, as measured by ΔV and calculated for μ_p, yielded additional information on the behavior of the adsorbed poly(organosiloxanes). (a) The linear portions of the μ_p *vs.* A curves confirmed that at high areas per monomer the chains undergo essentially no reorientation until they are compressed into a close-packed array. (b) Whereas the largest absolute values of the ΔV *vs.* A curves of the *n*-alkyl-substituted siloxanes indicated helix formation and subsequent coil compression, the largest absolute values of the 3,3,3-trifluoropropyl-substituted siloxanes indicated buckling and initial helix formation only. (c) Both ΔV and μ_p values had positive values for the *n*-alkyl-substituted polymers but had negative values for for the 3,3,3-trifluoropropyl-substituted polymers, indicating that the negative end of the monomeric dipoles of the latter were directed away from the water. It is concluded that the difference in sign of μ_p, as well as magnitude, point to a major difference in the biochemical and medical properties of these two classes of poly-(organosiloxanes).

We were also able to compute the value of $\mu_{p(\mathrm{CF_3})}$, where the CF_3 group is terminally attached to an alkyl segment, as approximately −0.5 D when the polymer molecule is adsorbed on the water surface in a condensed state.

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(28) W. L. G. Gent, *Quart. Rev., Chem. Soc.*, 2, 383 (1948).
(29) R. S. Holland and C. P. Smyth, *J. Amer. Chem. Soc.*, 77, 268 (1955).