

Figure 8. Model of the adsorption of water on HAP.

and lone-pair electrons of its oxygen atom attached to the various sites in the latter case. The absorbance of the a band increased until the BET monolayer capacity of 1.1 mmol g<sup>-1</sup> was reached but stayed constant above this water content. The reason for this result could be that these free OH groups exist only on the surface of adsorbed layers or

may remain inside the layer without hydrogen bonding. A band at 3691 cm<sup>-1</sup> in spectrum 4 of Figure 6 appeared simultaneously with band a. Therefore, this 3691-cm<sup>-1</sup> band may be the fundamental stretching vibration band of adsorbed water, since the wavenumber of this band is close to those of the fundamental stretching vibration of water vapor at 3756 and 3652 cm<sup>-1</sup>.<sup>22</sup> A model of the configuration of the surface P-OH groups and adsorbed water is postulated in Figure 8, as a summary of the discussion described above.

Registry No. Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, 12167-74-7.

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## Spreading Transition of a Liquid Film

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Liquids of poly(phenylmethylsiloxane) spread at the air-water interface undergo, with increasing temperature, a transition from the spread to the nonspread state. This was manifested as a vanishing of the surface pressure,  $\pi$ . It was also visualized. In spreading from a droplet of macroscopic size, i.e., from an essentially infinite reservoir,  $\pi$  vanished at  $55 \pm 2$  °C for a liquid with number-average molecular weight  $M_n = 2240$  g·mol<sup>-1</sup>. However, when the amount spread was limited to 2 and 1 mg·m<sup>-2</sup>, the temperatures at which the surface pressure vanished were  $42$  and  $37 \pm 2$  °C, respectively. The same pattern held, but at higher transition temperatures, for a liquid species with  $M_n = 1470$  g·mol<sup>-1</sup>. The dependence on the amount spread might be owing to molecular weight distribution in the polymer fractions but might also reflect increased equilibrium film thickness when the spreading coefficient is small (a "pancake"), as predicted by Joanny and de Gennes but apparently not previously observed. In this system, it is possible by varying the temperature to tune the spreading coefficient so that it passes continuously from positive to negative.

### Introduction

If a drop of nonvolatile liquid is placed onto a liquid or solid surface, there are three possibilities: it may spread completely to wet the substrate (form a film of zero contact angle), it may partially wet the substrate (form a film of finite contact angle), or it may dissolve. If the liquid is immiscible then only the first two possibilities remain. Which possibility occurs can be expressed as the outcome of competition between macroscopic interfacial energies described by the spreading coefficient.<sup>1</sup> Qualitatively, wetting reflects preferential adsorption of the spreading liquid to the interface, while partial wetting reflects preferential contact between the two other phases. Recent interest in these ancient questions has focused on the dynamics of spreading and on the transition between complete and partial wetting as the chemical potential is varied. The state of the art is discussed in recent reviews.<sup>2,3</sup>

On the experimental side, the wetting transition has been studied in detail for a handful of experimental systems.<sup>2,3</sup> But from experiment, little is known about the familiar physical situation, the spreading of a liquid droplet. The problem is to find a suitable experimental system.

Earlier<sup>4</sup> we reported measurements of surface pressure as a function of surface coverage for poly(phenylmethylsiloxane) liquids spread at the water-air interface at 22.8 °C. The behavior was unlike that characteristic of conventional amphiphiles such as pentadecanoic acid, for which the amphiphilic groups of the molecule are separated from the other end of the molecule, and layers beyond the monolayer do not form.<sup>1</sup> For liquids of number-average molecular weight  $M_n = 1470$  and  $2240$  g·mol<sup>-1</sup>, smooth transitions to multilayers and eventually films of macroscopic thickness was observed. It was concluded that these films wet the water-air interface. However, fractions of this polymer of higher molar mass failed to spread. This "drying" transition<sup>5</sup> as a function of molar mass, i.e., a transition from preferential wetting of water by liquid to its preferential wetting by air, is reminiscent of the observation, for linear hydrocarbons, that pentane, hexane, and heptane spread at the water-air interface but octane

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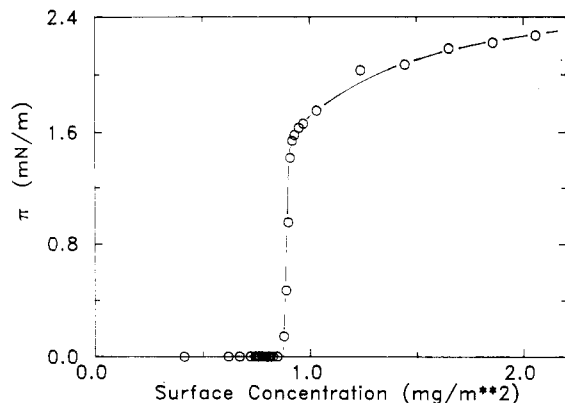
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**Figure 1.** Surface pressure at 10.0 °C plotted against surface concentration of polymer A.

does not.<sup>6</sup> It is also related to the classic experiments of Zisman in which the contact angle for the homologous series of liquids spread at solid-air interfaces was found to extrapolate to zero with decreasing molar mass.<sup>7</sup> Unfortunately, the above transitions, controlled by molar mass of the spreading liquid, vary discretely—just as does the molar mass.

We report here further experiments on the poly(phenylmethylsiloxane) system, from which it is concluded that a spreading transition occurs, even for the same molar mass liquid, when the temperature is varied. It therefore appears possible to tune the spreading coefficient *continuously*.

### Experimental Section

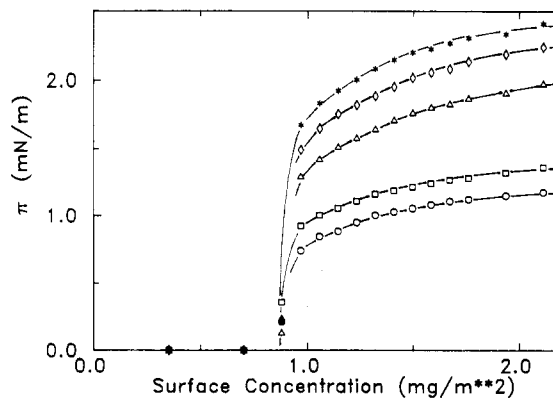
Experiments were performed at the University of Illinois. The experimental methods have been described in detail previously.<sup>8</sup> In brief, surface pressure was measured by the Wilhelmy plate method using a sand-blasted platinum foil. Experiments were performed inside a Teflon trough mounted within a thermostated chamber. The water was distilled and deionized before use. Dilute polymer solutions were prepared by weight in distilled chloroform or benzene (findings were the same using either solvent), and the surface pressure  $\pi$ , the amount by which the water surface tension was reduced by spreading of polymer to a known surface concentration  $c$ , was inferred from the lessened vertical force per length on an electronic balance after the films were spread and the spreading solvent had evaporated. The resolution in  $\pi$  was 0.01 mN·m<sup>-1</sup>.

The linear poly(phenylmethylsiloxane) (PPMS) was synthesized at the University of York and was methyl-terminated. The synthesis, fractionation, and characterization procedures have been reported.<sup>9</sup> <sup>1</sup>H NMR shows the PPMS fractions to be stereochemically atactic.<sup>10</sup> PPMS is immiscible in water and is non-volatile.

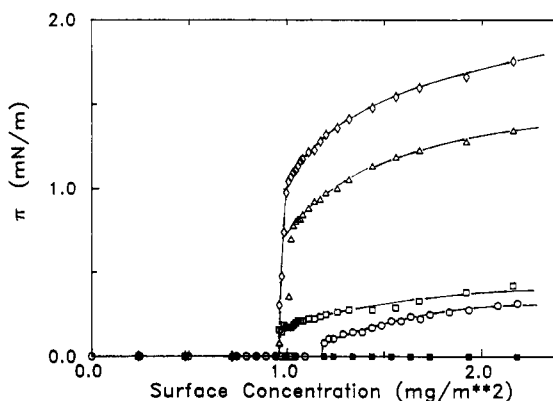
The two samples used in this study had number-average molecular weights  $M_n = 1470$  and 2240 and ratios  $M_w/M_n = 1.09$  and 1.08, respectively. The number-average degrees of polymerization are 11 and 16. The samples are referred to below as polymer A and polymer B, respectively.

### Results

In Figure 1, the surface pressure  $\pi$  is plotted as a function of surface concentration for polymer A ( $M_n = 1470$ ) at 10.0 °C. Even the highest surface pressures are



**Figure 2.** Surface pressure of polymer A plotted against surface concentration at various temperatures: (\*) 8.3, (◇) 13.0, (△) 18.4, (□) 28.6, (○) 33.8 °C.



**Figure 3.** Surface pressure for polymer B plotted against surface concentration at various temperatures: (◇) 6.0, (△) 12.2, (□) 32.1, (○) 35.4, (■) 37.3 °C.

exceptionally low, approximately one-tenth those typical<sup>1</sup> of spread polymer films. No surface pressure was measurable at  $c < 0.86$  mg·m<sup>-2</sup>, but thereafter  $\pi$  jumped abruptly. Molecular models show that the concentration  $c = 0.86$  mg·m<sup>-2</sup> (3.8 repeat units/nm<sup>2</sup>, i.e., 26 Å<sup>2</sup>/repeat unit) is consistent with a close-packed monolayer.

Note that at a surface concentration just below the step  $\pi$  is at least 2 orders of magnitude below the ideal gas prediction ( $\pi = CRT \approx 0.8$  mN·m<sup>-1</sup>). This strongly suggests a state of phase equilibrium between 2D islands of aggregated molecules and a low density of molecules in the gaseous state. The step in  $\pi$  at higher surface coverage is interpreted to reflect the low compressibility of the complete monolayer film. This phase diagram resembles qualitatively that reported and interpreted in detail previously<sup>4</sup> for other experiments performed at 22.8 °C. As discussed,<sup>4</sup> these films appear to spread over the surface smoothly no matter how much has been added; i.e., the films appear to have wet the water surface. In this system, because of phase separation at submonolayer coverages, a film covering the surface completely appears to be required to produce a surface pressure larger than  $0.01 \pm 0.01$  mN·m<sup>-1</sup>.

Measurements for polymer A at five additional temperatures ranging from 8.3 to 33.8 °C are shown in Figure 2. These isotherms all resemble that shown in Figure 1 with respect to displaying a pronounced step, but the magnitudes of  $\pi$  in the multilayer region fall decidedly with increasing temperature. At  $c = 2$  mg·m<sup>-2</sup>, between 8.3 and 33.8 °C, the surface pressure has fallen by a factor of 2.

For polymer B, of higher molar mass, the measurements shown in Figure 3 are qualitatively similar. However, the quantitative levels of surface pressure in the multilayer

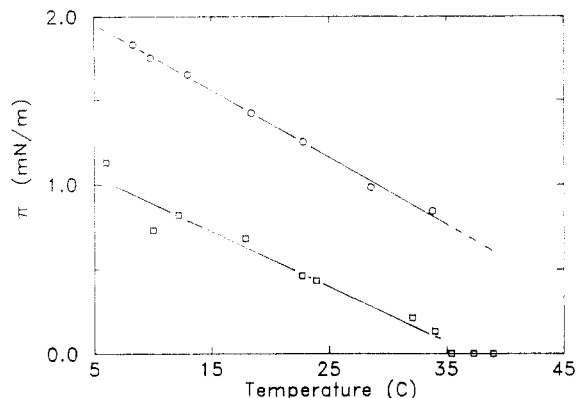
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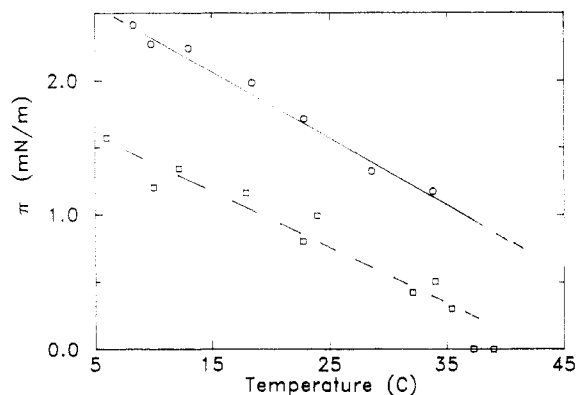
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**Figure 4.** Surface pressure at a fixed surface concentration of  $1 \text{ mg}\cdot\text{m}^{-2}$  plotted against temperature: (O) polymer A; (□) polymer B.



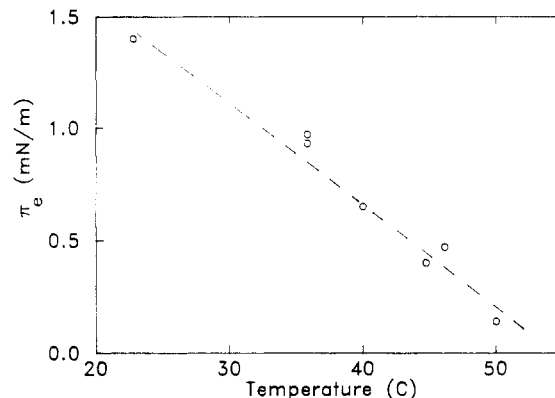
**Figure 5.** Surface pressure at a fixed surface concentration of  $2 \text{ mg}\cdot\text{m}^{-2}$  plotted against temperature. Symbols same as Figure 4.

region are approximately  $1 \text{ mN}\cdot\text{m}^{-1}$  lower at every surface coverage than for polymer A. With increasing temperature  $\pi$  falls, to the point that eventually no surface pressure could be detected.

Also in Figure 3, one has the first indication that the transition temperature depended on the amount of liquid added to the surface. Note that in the measurements made at  $35.4^\circ\text{C}$  the position of the step in  $\pi$  lay at 20% higher surface coverage than at the lower temperatures. This suggests that 20% additional mass was required to cover the surface with a continuous film. This is a result suggestive of the prediction,<sup>11</sup> not previously observed to our knowledge, that when the spreading coefficient  $S$  is low the equilibrium state is thicker than a monomolecular film.

Graphs of the temperature dependence of surface pressure, at constant mass of polymer on the surface, are shown in Figures 4 and 5. In Figure 4, this is shown at  $c = 1 \text{ mg}\cdot\text{m}^{-2}$ ; in Figure 5 it is shown at  $2 \text{ mg}\cdot\text{m}^{-2}$ . The temperature coefficient of  $\pi$  is linear within experimental uncertainty at both coverages. At surface coverages of 1 and  $2 \text{ mg}\cdot\text{m}^{-2}$  it is somewhat larger for polymer A ( $-0.040$  and  $-0.052 \text{ mN}\cdot\text{m}^{-1}\cdot\text{deg}^{-1}$ , respectively) than for polymer B ( $-0.032$  and  $-0.039 \text{ mN}\cdot\text{m}^{-1}\cdot\text{deg}^{-1}$ , respectively). As discussed below, these numbers are proportional to the differential surface entropy.

The temperatures at which  $\pi$  extrapolated to zero clearly were higher, the larger the quantity of polymer on the



**Figure 6.** Equilibrium film pressure for polymer B plotted against temperature.

surface. For example, at the respective concentrations of 1 and  $2 \text{ mg}\cdot\text{m}^{-2}$ , the extrapolated transition temperatures were  $53$  and  $56 \pm 2^\circ\text{C}$  for polymer A and  $37$  and  $42 \pm 2^\circ\text{C}$  for polymer B.

In a limited number of experiments, the equilibrium film pressure  $\pi_e$  from spreading a drop of undiluted polymer was measured. The mass spread was sufficient to produce a film thousands of layers thick. The measured surface pressures for polymer B, shown in Figure 6, are approximately 50% higher than those measured at the coverage of  $2 \text{ mg}\cdot\text{m}^{-2}$  (roughly two monolayers). They decrease with temperature with slope  $-0.046 \text{ mN}\cdot\text{m}^{-1}\cdot\text{deg}^{-1}$  and extrapolate to  $\pi = 0$  at  $55 \pm 2^\circ\text{C}$ .

However, the surface pressures  $\pi_e$  were not fully stable (as  $\pi$  was at the lesser surface coverages) but rose slowly (ca.  $0.005$ – $0.01 \text{ mN}\cdot\text{m}^{-1}\cdot\text{min}^{-1}$ ) over about 30 min. In principle this could have reflected slow kinetics of spreading. That possibility was ruled out by first sprinkling talc powder onto the clean water surface, depositing a polymer droplet, and verifying that the talc was swept immediately to the sides of the trough by the advancing film.

The instability in  $\pi_e$  and the higher transition temperature might result from fractionation of the polymer. Since fractions of lesser molar mass clearly are associated with higher  $\pi$  (cf. Figures 2 and 3), the observed rise in  $\pi_e$  might have resulted from migration of low molar mass fractions from the interior of the thick films to the interfaces. Even if these fractions comprised a small minority of the total sample added, they could suffice to saturate the interface. For example, a 1% minority of a droplet weighing  $1 \text{ mg}$  would suffice to cover an area of approximately  $100 \text{ cm}^2$  with a monolayer film. In view of this uncertainty, the data shown in Figure 6 for polymer B may not be comparable to the data for polymer B shown in Figures 3–5, although we emphasize that both sets of data do indicate clearly the vanishing of surface pressure with increasing temperature.

That this corresponded to a spreading transition was corroborated by experiments in which films of polymer B were visualized. Inert baked talc powder was sprinkled onto films spread at ca.  $33^\circ\text{C}$ . Upon a rise in temperature, the talc was observed to retract into numerous circular clumps upon the surface. Upon a lowering of the temperature these clumps redispersed, showing that the transition was reversible. The thin polymer films appeared to adsorb onto the talc powder so that the powder served as a marker for the presence of film.

## Discussion

It may be surprising that the poly(phenylmethylsiloxane) molecule, which is largely hydrophobic, should

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spread as a monolayer at all. However, experience shows that a material spreads owing to a delicate competition between affinity and antipathy for the liquid substrate.<sup>1,14</sup> In this instance, it is plausible to suppose that the polar siloxane backbone encourages spreading and that the two relatively hydrophobic side groups discourage it. It is known that a polymer of related chemistry, poly(dimethylsiloxane) (PDMS), also spreads at the water-air interface, with absolute levels of surface pressure 1 order of magnitude larger than in the present instance but with similar magnitudes of the temperature coefficient of surface pressure.<sup>14</sup>

For a film of macroscopic thickness, the origin of a spreading transition with increasing temperature can be understood. Recall that the experimental determination of  $\pi$  amounts to measuring the reduction of surface tension from that characteristic of the water-air interface. When a film of macroscopic thickness covers the water,  $\pi$  reflects a film with two well-defined noninteracting interfaces, water-polymer and polymer-air. Let us define  $\sigma_{W-A}$ ,  $\sigma_{W-P}$ , and  $\sigma_{P-A}$  to be the interfacial tensions of the water-air, water-polymer, and polymer-air interfaces, respectively. Then from the method of measurement

$$\pi_e = \sigma_{W-A} - [\sigma_{W-P} + \sigma_{P-A}] \quad (1)$$

The right-hand side of this equation is also an expression for the well-known spreading coefficient,  $S$ .<sup>1</sup>  $S > 0$  corresponds to complete wetting,  $S < 0$  to partial wetting. The transition to  $\pi = 0$  signifies the transition to a zero (and subsequently negative) spreading coefficient.

The decrease of  $\pi_e$  with increasing temperature, eventually the decrease to zero, could then follow from the temperature dependence of the interfacial tensions in question. These are known to be approximately  $-0.13 \text{ mN}\cdot\text{m}^{-1}\cdot\text{deg}^{-1}$  for  $\sigma_{W-A}$  near room temperature<sup>12</sup> and  $-0.11 \text{ mN}\cdot\text{m}^{-1}\cdot\text{deg}^{-1}$  for  $\sigma_{P-A}$ .<sup>15</sup> The temperature derivative of  $\sigma_{W-P}$  is unfortunately not known, and to measure it was not possible with the equipment available in our laboratory. If it were such that the terms inside the parenthesis in eq 1 would have a temperature derivative less negative than the term outside,  $\pi_e$  would decrease with increasing temperature.

In interpreting the spreading transition of thinner films, interactions between the two interfaces<sup>11</sup> would of course need to be included in eq 1. In view of uncertainties discussed below, no quantitative treatment is attempted at this time.

Joanny and de Gennes<sup>11</sup> have predicted that the equilibrium film thickness of a film spread onto a limitless area will be larger than monomolecular if the spreading coefficient  $S$  is sufficiently small. This is owing to a competition between long-range forces, which tend to maintain a thicker film, and spreading; sufficiently small  $S$  is too weak to deliver the expense of energy required to squash molecules down to a monolayer. A "pancake" forms instead. In the present experiments, when the spreading coefficient is sufficiently low—or, as discussed above, when the surface pressure  $\pi_e$  is sufficiently low—larger amounts of polymer should be required to cover a given surface area with a continuous film as opposed to when the spreading coefficient is larger. Indeed, the temperatures at which  $\pi$  vanished were observed to vary in this manner. The

observations are thus in qualitative agreement with the possibility of pancake formation at low spreading coefficient.

However, it is also the case that the molecular weight distribution in the polymer samples could have resulted in fractionation at the interfaces, as noted in the Results section. Although the present samples were narrow in molecular weight distribution, some distribution is inevitable. To the extent that a minority of species of high molecular weight failed to spread,<sup>4</sup> a larger total mass of polymer would be required to cover the surface with spread film than would have been required at lower temperatures where such fractionation did not occur. Further work will be required to clarify the relative importance of these two influences, which could both have contributed in the present experiments.

The temperature coefficient of the surface pressure is proportional to the derivative of surface entropy with surface concentration, as pointed out long ago by Harkins.<sup>13</sup> The derivation is straightforward. A negative temperature coefficient of surface pressure, as in the present experiments, implies that entropy increased with increasing surface concentration. This reasonable result is consistent with a gain of entropy as the semiflexible polymer chains acquire degrees of freedom by collapse to the three-dimensional state.

These experiments suggest, but clearly do not conclusively prove, that the transition in  $\pi$  was first order. Although it is suggestive to note, in Figures 4 and 5, that the extrapolated straight lines for polymer B extend beyond points at which  $\pi = 0$  was measured directly, unfortunately this extrapolation is not far beyond the bounds of experimental uncertainty. The scatter in measurements of  $\pi$  (lower than may appear, considering the low absolute values of  $\pi$ ) could not be reduced with our present experimental setup.

## Conclusion

The chief finding of the above experiments is that surface pressure decreased, to the point of vanishing within experimental uncertainty, upon raising the temperature. It appears that this system undergoes a spreading transition not only with increasing molar mass<sup>4</sup> but also with increasing temperature. This is a "drying" transition:<sup>2,3,5</sup> a transition from preferential wetting of the substrate by added liquid to its preferential wetting by air. In this system, it appears possible to tune the spreading coefficient so that it passes continuously from positive to negative.

The observations may provide experimental support for the theoretical prediction of "pancake" formation,<sup>11</sup> i.e., increased equilibrium film thickness, when the spreading coefficient is small. The evidence in favor is that the transition temperature rose with increasing amounts of liquid spread. As discussed above, further work will be necessary to clarify the relative contributions of molecular weight distributions in the polymer samples and of possible pancake formation.

This transition of a liquid droplet from spread to droplet opens many possibilities for more microscopic experiments than the present ones. In addition, the source of the transition in the temperature dependence of interfacial tensions may afford a strategy for identifying other such systems.

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