

which upon substitution of eq 13c for  $q$  becomes

$$2(u^* - 1) + (2 - u^*)(1 - u^*)^{1/2} = 0 \quad (\text{D.8})$$

The only value of  $u^*$ ,  $0 < u^* \leq 1$ , which satisfies this equation is  $u^* = 1$ .

## References and Notes

- (1) Flory, P. J. *J. Am. Chem. Soc.* 1941, 63, 3083, 3091, 3096.
- (2) Stockmayer, W. H. *J. Chem. Phys.* 1943, 11, 45.
- (3) Gordon, M. *Proc. R. Soc. London, Ser. A* 1962, 268, 240.
- (4) Gordon, M.; Scantlebury, G. R. *Trans. Faraday Soc.* 1964, 60, 604.
- (5) Gordon, M.; Dobson, G. R. *J. Chem. Phys.* 1964, 41, 2389.
- (6) Gordon, M.; Parker, T. G. *Proc. R. Soc. Edinburgh* 1970/1971, 69, 13.
- (7) Gordon, M.; Ross-Murphy, S. B. *Pure Appl. Chem.* 1975, 43, 1.
- (8) Good, I. J. *Proc. R. Soc. London, Ser. A* 1963, 272, 54.
- (9) Falk, M.; Thomas, R. E. *Can. J. Chem.* 1974, 52, 3285.
- (10) Macosko, C. W.; Miller, D. R. *Macromolecules* 1976, 9, 199, 206.
- (11) Dusek, K. *Polym. Bull.* 1979, 1, 523.
- (12) Ziff, R. M. *J. Stat. Phys.* 1980, 23, 241.
- (13) Ziff, R. M.; Stell, G. *J. Chem. Phys.* 1980, 73, 3492.
- (14) Donoghue, E.; Gibbs, J. H. *J. Chem. Phys.* 1979, 70, 2346.
- (15) Donoghue, E. *J. Chem. Phys.* 1982, 77, 4236.
- (16) Donoghue, E. In "Kinetics of Aggregation and Gelation", Family, F., Landau, D. P., Eds.; North-Holland Publishing Co.: Amsterdam, 1984; p 221.
- (17) Cohen, R. J.; Benedek, G. B. *J. Phys. Chem.* 1982, 86, 3696.
- (18) van Dongen, P. G. J.; Ernst, M. H. *J. Stat. Phys.* 1984, 37, 301.
- (19) Spouge, J. L. *Can. J. Chem.* 1984, 62, 1262.
- (20) Miller, D. R.; Macosko, C. W. *Macromolecules* 1980, 13, 1063.
- (21) Wiegel, F. W.; Perelson, A. S. *J. Stat. Phys.* 1982, 29, 813.
- (22) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
- (23) Goldstein, B.; Perelson, A. S. *Biophys. J.* 1984, 45, 1109.
- (24) van Dongen, P. G. J.; Ernst, M. H. In "Kinetics of Aggregation and Gelation", Family, F., Landau, D. P., Eds.; North-Holland Publishing Co.: Amsterdam, 1984; p 205.

## Surface Pressure of Linear and Cyclic Poly(dimethylsiloxane) in the Transition Region

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**ABSTRACT:** Surface pressure  $\pi$  has been measured as a function of surface concentration  $c$  for monolayers of linear and cyclic poly(dimethylsiloxane) (PDMS) of molecular weight 730–14 800, spread on water and tricresyl phosphate at 26.0 °C. In the transition region where the surface pressure rises much more rapidly than proportional to the surface concentration, the findings for linear and cyclic PDMS were indistinguishable and independent of molecular weight. The findings in this region could be described as power laws with powers corresponding to scaling predictions for the semidilute region of concentrations (coil overlap accompanied by low overall polymer concentration) on near- $\Theta$  and fairly good surface solvents, respectively. However, the second virial coefficient of the surface pressure appeared to be negative for both liquid supports. These observations, the fact that the transition region occurred at quite high fractional surface coverage, and the instability of films from small oligomers suggest that recent interpretations of behavior in the transition region in terms of predictions for a semidilute surface solution are invalid in this case. The existence of a semidilute region of concentrations for polymer monolayers is uncertain in principle. In addition, the comparisons of linear and cyclic polymer above the overlap concentration  $c^*$  lead to the surprising conclusion that even for three-dimensional semidilute solutions, the ratio  $c/c^*$  is not a universal reduced concentration.

## Introduction

When an uncharged amorphous high polymer is spread on a liquid support to form a monolayer, a surface pressure exists that is analogous to the osmotic pressure characteristic of three-dimensional solutions. Surface pressure is the amount by which the surface tension is reduced from that of the pure liquid. The dependence of the surface pressure on surface concentration is simpler than that found for many small molecules;<sup>1,2</sup> three regions can be qualitatively distinguished. In the dilute region, molecules interact sufficiently little that the surface pressure can be described by the first few terms of a virial expansion. The surface pressure in this region depends on the density of molecules, and hence on the molecular weight. At concentrations that correspond approximately to full coverage of the surface by polymer, there begins a plateau of relatively constant surface pressure. This is generally interpreted to reflect collapse of the monolayer to a three-dimensional state. Between these extremes, a transition region is observed. Here the surface pressure rises much

more rapidly than proportional to the surface concentration and is independent of molecular weight.

In the transition region, the surface pressure  $\pi$  has been found to follow a power-law dependence on the surface concentration  $c$  of polymer.<sup>3–5,52</sup> This behavior has been interpreted<sup>3–5,52</sup> as reflecting a scaling law<sup>6,7</sup> for a semidilute region:

$$\pi/RT = kc^m \quad (1)$$

Here  $R$  is the gas constant,  $T$  the absolute temperature,  $k$  a prefactor of unspecified magnitude, and  $m$  a power that depends on the quality of what is considered to be the surface solvent. The value of  $m$  is  $2\nu/(2\nu - 1)$ , where  $\nu$  is the power of molecular weight to which a two-dimensional polymer coil's radius of gyration is proportional at infinite dilution. The power  $\nu$  is thought to be approximately 0.75 on a good solvent<sup>8</sup> and approximately 0.505 on a  $\Theta$  solvent.<sup>9</sup> The surface pressure should thus be proportional to approximately the 3rd power of surface concentration when the polymer is spread on a good surface solvent and approximately the 101st power when it is spread on a  $\Theta$  solvent. Water at 16.5 °C was thus inferred to be a good surface solvent for poly(vinyl acetate) and nearly a  $\Theta$  solvent for poly(methyl methacrylate),<sup>3</sup> while a transition from  $\Theta$  solvent to good solvent was reported for water

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**Table I**  
**Characterization of the Linear and Cyclic PDMS Samples**

| code | linear                       |                   | cyclic |           |
|------|------------------------------|-------------------|--------|-----------|
|      | $M_n$                        | $M_w/M_n$         | $M_n$  | $M_w/M_n$ |
| A    | 890                          | 1.01              | 730    | 1.07      |
| B    | 1670                         | 1.01              | 1480   | 1.02      |
| C    | 6330                         | 1.17              | 5430   | 1.03      |
| D    | 14800                        | 1.11              | 14500  | 1.03      |
| E    | $9 \times 10^6$ <sup>a</sup> | <1.2 <sup>b</sup> |        |           |

<sup>a</sup> Calculated from  $M_w$  measured<sup>31</sup> by light scattering.

<sup>b</sup> Measured<sup>32</sup> by GPC for similar samples.

bearing poly(methyl acrylate) in a narrow range of temperatures above 18.2 °C.<sup>4,5</sup> Water at 22 °C was inferred to be a good solvent for poly(ethylene oxide) and poly(tetrahydrofuran).<sup>52</sup> For poly(vinyl acetate) on water small deviations from power law behavior have also been observed, however.<sup>10</sup>

It is puzzling that predictions for a semidilute region of concentrations (coil overlap accompanied by low overall polymer concentration)<sup>6,7</sup> have described these findings, since power-law behavior appears to persist to high coverages of the surfaces by polymer (see discussion below). Equation 1 has till present been applied to the behavior of linear species spread on water. Poly(dimethylsiloxane) (PDMS) exists in both linear and cyclic forms and has been reported to form a monolayer on several hydrocarbon liquids<sup>11–13</sup> as well as on water.<sup>14–17</sup> In the study described here, measurements were made of the surface pressures of linear and cyclic PDMS in the dilute as well as the transition region, on two liquid supports. The findings appear to appear to be inconsistent with a description by means of eq 1.

## Experimental Section

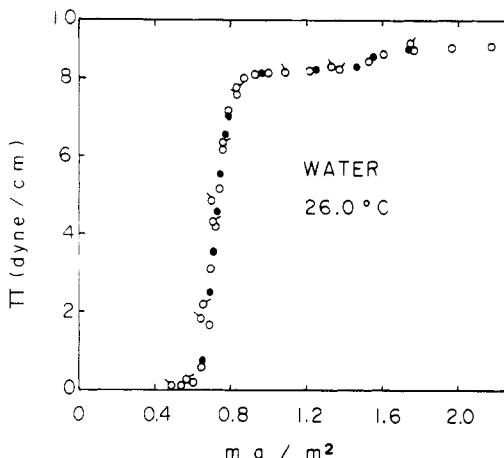
**Materials.** Fractions of linear and cyclic poly(dimethylsiloxane) were generously donated by Dr. J. A. Semlyen and Dr. S. J. Clarsen of the University of York. The synthesis<sup>18–20</sup> and purification for monolayer experiments<sup>21</sup> have been described previously. Characterization was by gas-liquid chromatography (polymers A and B) and analytical gel permeation chromatography (polymers C and D). Number-average molecular weights  $M_n$  and ratios  $M_w/M_n$  of weight-average to number-average molecular weight are listed in Table I.

The simple ring structures of the cyclic polymers have been confirmed by measurements of their intrinsic<sup>18</sup> and bulk<sup>22</sup> viscosities, small-angle neutron scattering,<sup>23,24</sup> quasi-elastic light scattering,<sup>25</sup> diffusion measurements,<sup>26–29</sup> and <sup>29</sup>Si nuclear magnetic resonance.<sup>30</sup>

An additional sample of extremely high molecular weight linear PDMS, polymer E in Table I, was generously donated by Dr. S. Boileau of the Collège de France and Professor C. W. Macosko of the University of Minnesota.

Water and tricresyl phosphate (Fluka) were used as liquid supports. Their surface tensions at 26.0 °C, measured by the de Noüy ring method using the corrections of Harkins and Jordan,<sup>33</sup> were 71.77 and 37.71 dyn/cm, respectively. The water (thrice distilled) was distilled shortly before use, but the tricresyl phosphate, a mixture of isomers, was used as received in view of its toxicity upon thermal decomposition. As discussed below, the tricresyl phosphate nonetheless appeared to contain negligible amounts of surface-active contaminants.

**Spreading Solutions.** Spreading solutions of the polymers were prepared by weight in hexane, chloroform, and benzene at concentrations between 0.05 and 0.5 mg/mL. These solvents were spectroscopic grade (Merck) and were used as received. An Agla microsyringe driven by a micrometer head was used to deposit the spreading solutions onto the liquid supports, typically in 2–6-μL aliquots. The surface pressures quickly returned to zero when the pure solvents were spread. Thus it seems that the small quantities of spreading solvents which may have dissolved in the liquid supports did not affect the measurements and also that



**Figure 1.** Surface pressure at 26 °C of water bearing linear polymer D plotted against surface concentration of polymer. Points: (○) area compressed after spreading polymer from chloroform solution; (●) area expanded following the compression indicated by open circles; (◐) area compressed after spreading from hexane solution; (○) surface concentration changed at fixed area by successively adding aliquots of chloroform solution.

the spreading solvents were essentially free of nonvolatile surface-active impurities.

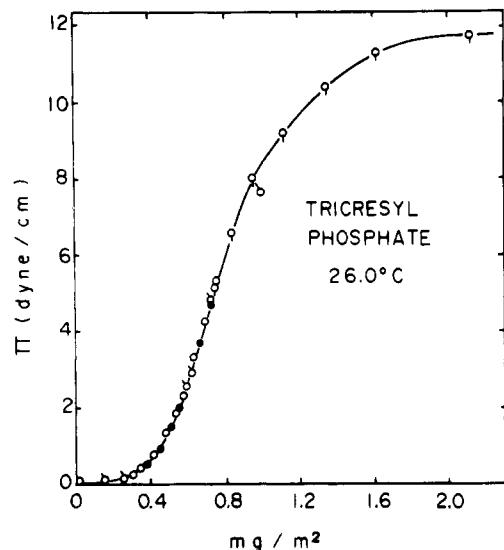
**Surface Pressure Measurements.** Experiments were carried out at 26.0 °C in the thermostated Teflon-coated trough provided with a Lauda film balance. The Wilhelmy plate method of surface pressure measurement was generally used, although isolated direct measurements were also made by the Langmuir method to verify that the contact angle of tricresyl phosphate on the Wilhelmy plate was zero. For Wilhelmy plate measurements, a sand-blasted platinum plate 2 cm long was suspended from an HBM Model Q11 LVDT transducer, and the output was measured by a voltmeter after passage through an HBM Model KWS3073 amplifier. Measurements in independent experiments were reproducible to better than 0.05 dyn/cm when the surface pressure was less than 1 dyn/cm and were somewhat less reproducible at higher surface pressures; the discrepancies are ascribed to changes in the instrumental zero described below. For measurements by the Langmuir method, the Lauda film balance was used, modified so that the detection barrier was rigidly attached to the deflection spring rather than floating on the liquid surface.

Tricresyl phosphate tended to climb the platinum plate by capillary action, increasing the weight of the plate and generating fictitious surface tension. To minimize this, all measurements were made with the plate submerged except for a few millimeters, and its stem tightly bound with Teflon tape. Errors of several dyn/cm resulted when these precautions were not taken.

The surface concentration of polymer was almost always varied by successive compression. The equilibration time at a given area was a few seconds on water. Probably because of slow diffusion on the surface, it was as long as 15 min on tricresyl phosphate when the surface pressure was low. Typically the surface was compressed a factor of 14, starting from an initial area of 800 cm<sup>2</sup>. The quantity of polymer deposited was typically on the order of 20 μg. It was verified that the measurements did not depend on the amount of polymer deposited. It was also verified periodically that the residual surface pressure on nominally clean surfaces, measured at a time corresponding to the duration of a typical experiment after the surface was cleaned, was less than 0.2 dyn/cm at maximum compression. On tricresyl phosphate this degree of cleanliness was much easier to achieve than on water.

## Results

**Reliability of the Experimental Results.** The reliability of the experimental results was tested extensively on both liquid supports. Figures 1 and 2 illustrate this for linear polymer D ( $M_n = 14800$ ) on water and tricresyl phosphate, respectively. Surface pressure  $\pi$  is plotted against surface concentration of polymer. The pressure-concentration curves do not depend on whether hexane



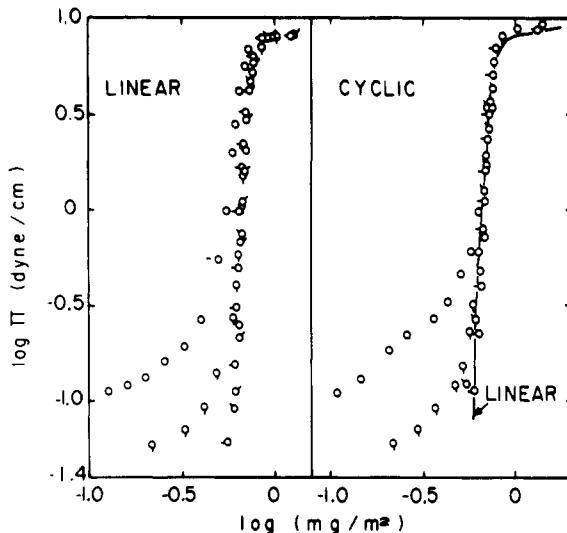
**Figure 2.** Surface pressure at 26 °C of tricresyl phosphate bearing linear polymer D plotted against surface concentration of polymer. Points: (○) area compressed after spreading polymer from hexane solution; (●) area expanded following the compression indicated by open circles; (□) area compressed after spreading from chloroform solution; (◇)  $\pi$  measured by Langmuir method and surface concentration changed at fixed area by successively adding aliquots of hexane solution.

or chloroform was used as the spreading solvent. In addition, the same results were obtained when the surface concentration was altered by changing the area available to a fixed amount of polymer, as by adding successive aliquots of polymer to a fixed surface area. Thus the results did not depend on the initial surface concentration of polymer deposited.

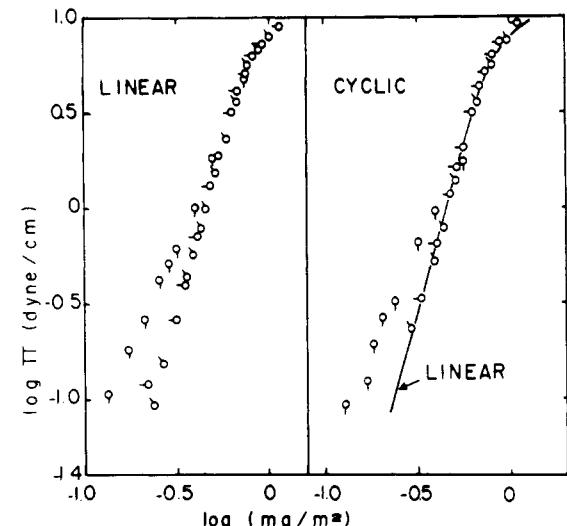
Reversibility of the measurements is also illustrated in Figures 1 and 2. On water, reversibility extended even far into the plateau region. On tricresyl phosphate, the measurements were quantitatively reversible up to the inflection point of the pressure-concentration diagram. It is evident that power-law behavior could not apply at concentrations past the inflection point. Experiments in the plateau region were also quantitatively reversible, but some irreversibility (on the order of 0.5 dyn/cm) appeared following expansion back to 5 dyn/cm.

On water, the surface pressures associated with polymers B and larger ( $M_n > 1700$ ) were stable in time. But on tricresyl phosphate, even the largest polymers displayed a slow decay of the surface pressure at a fixed nominal surface concentration, indicating some dissolution. At surface pressures of 5–7 dyn/cm (where the surface pressure is very sensitive to changes in surface concentration), the rate of decay of surface pressure was nearly linear in time, a factor of 0.01 per hour. Typical experiments (comprising measurements at many areas) lasted up to 2 h.

For the smallest oligomers, measurements were not reversible on either liquid support. On water, the rate of surface pressure decay of polymers A (approximately decamers) at 7 dyn/cm was a factor of 0.002 per minute, although (as noted) the surface pressure from polymers B (approximately eicosamers) was stable. On tricresyl phosphate, polymers A dissolved too rapidly for reliable measurements to be made, but measurements are reported below for polymers B, for which the rate of surface pressure decay at 7 dyn/cm was a factor of 0.001 per minute. These rates of dissolution were slow enough to permit short experiments in the very interesting dilute region, where the change in pressure with concentration is gradual. The



**Figure 3.** Surface pressure at 26 °C of water bearing linear and cyclic PDMS plotted logarithmically against surface concentration of polymer for PDMS of several molecular weights. Points: (○) polymers A; (□) polymers B; (◇) polymers C; (△) polymers D; (▽) polymer E.

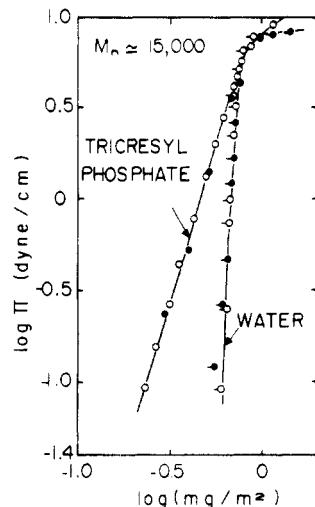


**Figure 4.** Surface pressure at 26 °C of tricresyl phosphate bearing linear and cyclic PDMS plotted logarithmically against surface concentration of polymer for PDMS for several molecular weights. Points: same as Figure 3.

accuracy of the measurements was checked by making repeated independent measurements, starting from different initial amounts of polymer deposited.

The pressure-concentration curves found in this study are in general agreement with those reported previously.<sup>13–17</sup> The solubility in water of small PDMS oligomers has been noted previously.<sup>16</sup> A discussion of the marked sensitivity of the positions of the curves for water to slight amounts of impurities will be reported elsewhere. The quantitative reliability of the present measurements is supported by the agreement found in the transition region between independent measurements on polymers of different molecular weights, as described below.

**Power-Law Behavior in the Transition Zone.** In Figures 3 and 4, surface pressure is plotted logarithmically against surface concentration of polymer for water and tricresyl phosphate, respectively, bearing PDMS of several molecular weights. The range of molecular weight is a factor of  $10^4$  on water and nearly 10 on tricresyl phosphate. The logarithmic representation shows clearly the demarcation between the dilute region, observed only for small



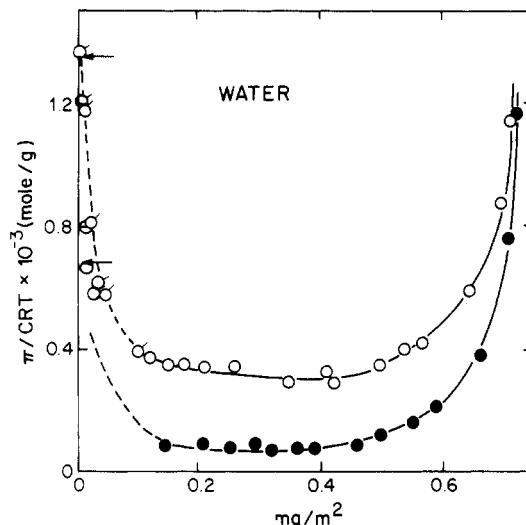
**Figure 5.** Surface pressure at 26 °C of water and tricresyl phosphate bearing linear (O) and cyclic (●) polymers D plotted logarithmically against surface concentration of polymer.

oligomers, and the transition region where there is no detectable dependence on molecular size. Figures 3 and 4 include comparisons of the findings for cyclic and linear molecules and show that in the transition region there is no detectable dependence on molecular geometry either. The onset of the plateau region, where the rate of surface pressure increase begins to slow down, can also be seen in Figures 3 and 4. It is apparent that the transition regions span only narrow ranges of surface concentration.

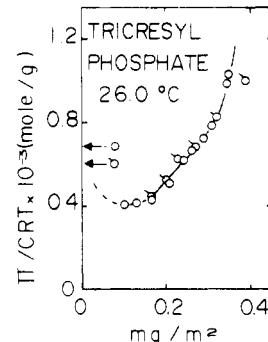
The findings for polymers D ( $M_n \approx 15,000$ ) have been assembled in Figure 5 for both liquid supports. The open circles, representing data for linear polymers, lie on the same curves as the filled circles, representing data for cyclic polymers. The onset of the plateau region falls at a similar concentration for both water and tricresyl phosphate. In the transition regions the data for water are consistent with a line of slope approximately 50, and the data for tricresyl phosphate with a line of slope 3.5, as expected from eq 1 for near- $\Theta$  and rather good surface solvents, respectively.

**Signs of the Second Virial Coefficients.** In efforts to extrapolate to infinite dilution as in previous reports,<sup>3-5,52</sup> measurements of the surface pressure were made for the small PDMS oligomers at the lowest surface concentrations for which reliable surface pressure measurements were possible. The findings are displayed in Figures 6 and 7 as virial plots of the reduced surface pressure  $\pi/cRT$  against the surface concentration  $c$ . Figure 6 (water) shows the behavior of cyclic oligomers A ( $M_n = 730$ ) and B ( $M_n = 1480$ ); the behavior of linear oligomers A and B was indistinguishable from that of their cyclic counterparts. Figure 7 (tricresyl phosphate) shows the behavior of cyclic and linear oligomers B. The same qualitative behavior is seen for the linear as for the cyclic oligomers. An influence of end effects on the measurements is of course conceivable for the cyclic oligomers.

Figure 6 includes measurements for cyclic polymer A at surface concentrations as low as 0.01 mg/m<sup>2</sup>, which is approximately 1% of full coverage of the surface by polymer. These measurements were made at the Forest Products Laboratory of the University of Minnesota with the kind assistance of Professor Ronald E. Neuman and Mr. Tom Tompkins. A Cahn electrobalance attached to a sand-blasted glass Wilhelmy plate was used to measure the surface pressure, and the ambient air temperature was controlled to 0.02 °C. The experimental precision was  $\pm 0.003$  dyn/cm. The apparatus will be described in more detail elsewhere.<sup>34</sup> Figure 6 shows clearly that at concen-



**Figure 6.**  $\pi/cRT$  of water bearing cyclic polymers A and B plotted against surface concentration of polymer. Points: (O)  $M_n = 730$  at 26 °C; (●)  $M_n = 1480$  at 26 °C; (O)  $M_n = 730$  at 20 °C as described in the text. Arrows indicate  $1/M_n$ .



**Figure 7.**  $\pi/cRT$  at 26 °C of tricresyl phosphate bearing linear (O) and cyclic (●) polymers B plotted against surface concentration of polymer. Arrows indicate  $1/M_n$ .

trations below 0.1 mg/m<sup>2</sup> (approximately 10% of surface coverage) the extrapolation to  $1/M_n$  expected in data approaching zero concentration<sup>35,36</sup> appears to hold, despite the polymer's finite solubility in water.

The chief finding in Figures 6 and 7 is that in every instance, the reduced surface pressure  $\pi/cRT$  descends to a value considerably less than the value  $1/M_n$  to which it must extrapolate. For cyclic polymer B the ratio of  $\pi/cRT$  to  $1/M_n$ , which would be unity for a  $\Theta$  solvent, descends to 0.6 on tricresyl phosphate and 0.1 on water. The observation that  $\pi/cRT$  descends below  $1/M_n$  suggests strongly that the second virial coefficients of PDMS on these liquid supports are negative.

On water, the discrepancy between the lowest value of  $\pi/cRT$  and  $1/M_n$  increases with increasing molecular weight, to the point that for polymers C, D, and E no surface pressure could be measured in the dilute region. As emphasized by Rondelez,<sup>37</sup> for polymers C, D, and E this may reflect phase separation in two dimensions.

## Discussion and Conclusions

**Nature of the Transition Region.** Measurements are presented above of the surface pressure  $\pi$  for surface films of linear and cyclic PDMS on two liquid supports. In the transition region where the surface pressure rises much more rapidly than proportional to the surface concentration, the findings for water and tricresyl phosphate could be described as power laws with powers corresponding to scaling predictions for the semidilute region on near- $\Theta$  and fairly good surface solvents, respectively. However, the

second virial coefficient of the surface pressure appeared to be negative for both supports.

The transition regions fell at rather high surface coverages. Apparent power laws held up to  $0.75 \text{ mg/m}^2$  on both liquid supports, and measurements were not made below surface concentrations of  $0.1 \text{ mg/m}^2$ . As inspection of Figures 1–5 as well as consideration of molecular models<sup>14,17</sup> shows, at  $1 \text{ mg/m}^2$  PDMS certainly covered the surfaces. Interpretation of power-law behavior in the transition zone by means of eq 1 would seem to imply that on the apparently good surface solvent tricresyl phosphate, PDMS coils remain swollen by excluded volume effects at a fractional surface coverage of 75%. However, as remarked by de Gennes,<sup>38</sup> predictions concerning a semidilute region should not apply unless the surface coverage is low. Theories for a semidilute region refer to concentrations which, while higher than the critical concentration  $c^*$  for polymer overlap, are sufficiently low that interactions between polymers are overwhelmed by the interactions of polymer with solvent.<sup>7</sup> It does not seem that this condition was satisfied in the present experiments. Power-law behavior at high surface coverage has also been found for other polymer monolayers.<sup>3–5</sup>

The solubility of films of small PDMS oligomers leads to considering the criterion for formation of a stable monomolecular film. Few high-polymer monolayers are known. Insolubility in the liquid substrate is not the criterion; polystyrene does not spread on water,<sup>45,46</sup> while poly(ethylene oxide) forms a stable monolayer despite its solubility in water in all proportions.<sup>46,47</sup> It has long been believed<sup>1,2</sup> that the criterion of spreadability, for high polymers as well as for small amphiphilic molecules, is a delicate competition between antipathy and affinity for the liquid support. Other amorphous, uncharged high polymers which form stable monolayers on water are PDMS, poly(methyl methacrylate),<sup>3</sup> poly(vinyl acetate),<sup>3</sup> poly(methyl acrylate),<sup>4,5</sup> and poly(tetrahydrofuran).<sup>52</sup> Here the chemistry of the monomeric units implies<sup>1,2</sup> that stable films are formed by virtue of a large aggregate free energy of adsorption but that the individual monomeric units adsorb only weakly to the surface. This leads to expecting desorption from a spread monolayer unless the molecular weight is sufficiently high. Whether solubility of oligomers implies that from monolayers of large polymers loops dip into solution, or whether merely segments of a very few monomeric units become submerged momentarily in a statistical fashion, is not known. Instability of surface pressure in films of poly(vinyl acetate) oligomers was reported long ago.<sup>48</sup> It is expected that small oligomers of other high polymers would be soluble as well. The tacit assumption<sup>3–5,52</sup> that high polymers in monolayers assume flat configurations with all segments directly at the liquid surface appears to be questionable.

In a strictly two-dimensional film, chains would never cross. It is intriguing that in the present experiments the variation of surface pressure with surface concentration was the same when surface concentration was increased by compression starting from low initial surface coverage, as by successive addition of polymer to a fixed surface area. Figures 1 and 2 illustrate this for linear polymers D; the same was found for polymer E ( $M_w = 9 \times 10^6$ ). When high polymer is added to a surface where the coverage already is high, the resulting chain configurations may include some random matting. One can speculate that surface pressure may not be sensitive to small amounts of chain crossing. To investigate the degree to which the monolayers may be matted and the fraction of monomeric units which ride directly at the liquid surface, in future work

it will be desirable to have more direct probes of surface structure than just the surface pressure.

It is interesting to consider the possibility of a semidilute surface solution in principle. In conventional three-dimensional solutions, a semidilute region of concentration can exist by virtue of the fact that the space pervaded by a sufficiently long polymeric string is so much larger than the space actually occupied. In two dimensions, the missing degree of freedom alters the matter considerably. Vilanova and Rondelez have estimated<sup>3</sup> that in a surface  $\Theta$  solvent, the critical overlap concentration  $c^*$  is independent of molecular weight and hence that a macroscopic melt exists already at  $c^*$ . It thus appears doubtful that semidilute concentrations could exist in a surface  $\Theta$  solvent. Although in a better solvent the situation should be less singular, the average segment density within individual polymeric coils will still be high even when the coils are on the average widely separated. Moreover, there appears to exist no evidence showing that the coils in polymer monolayers intertwine appreciably rather than occupy discrete domains on the surface. On all these grounds, the existence in a surface solution of a semidilute concentration region even at low surface coverages appears to be uncertain.

In seeking alternative equations of state than eq 1 to describe the present findings in the transition region, it emerges that the situation is difficult to describe quantitatively with a general theory. Singer's<sup>39</sup> lattice treatment for an athermal surface solution, the analogue of the Flory–Huggins<sup>40</sup> theory expressed for an athermal three-dimensional solution, was extended to include interaction energies by Ter Minassian-Saraga and Prigogine,<sup>41</sup> Motomura and Matuura,<sup>42</sup> and Huggins.<sup>43</sup> The possibility that loops of polymer dip into solution has also been considered.<sup>44</sup> A number of experimental studies over the years have shown that these theories describe behavior at low surface concentrations most successfully, unless the number of parameters is large. Given that the behavior of protein monolayers at higher concentrations resembles that of flexible amorphous polymers,<sup>1,39</sup> the presumption that a polymer's flexibility markedly influences the surface pressure may be doubtful. As will be discussed elsewhere, the experimental situation for PDMS on water has points in common with a two-dimensional solution of hard disks.

**Extrapolation to Infinite Dilution.** The measurements at low surface pressures reported in Figures 6 and 7 illustrate the difficulty of extrapolating surface pressure to infinite dilution unless the surface coverage is low. Quite misleading conclusions would have been reached had the oligomer molecular weights not been known independently. Motomura<sup>49</sup> emphasized long ago that even when the extrapolation from high surface coverage is apparently well-behaved,<sup>3–5,35</sup> the reasons may be much more complicated than can be interpreted by a single second virial coefficient.

**Comparison of Linear and Cyclic PDMS.** An additional aspect of these experiments is comparison of linear and cyclic PDMS. No quantitative interpretation is offered at this time of measurements in the dilute region (cf. Figures 6 and 7 and text), since they clearly reflect the influence of virial coefficients of higher order than the second. In the transition region, the surface pressures of linear and cyclic PDMS are indistinguishable at a given surface concentration. This behavior implies<sup>7</sup> that here the surface pressure reflects interactions of range shorter than molecular dimensions.

Cyclic molecules have a more compact average configuration than linear molecules of the same molecular

weight<sup>50,51</sup> and consequently a higher overlap concentration  $c^*$ . The relation  $c^* \propto 1/R_G^3$  in a three-dimensional solution<sup>7</sup> (where  $R_G$  is the radius of gyration) implies that  $c^*$  is higher by factors of approximately 2.3 and 2.8 in good and  $\Theta$  solvents, respectively. The paradoxical argument could then be made, in three dimensions as in two, that although equilibrium properties at concentrations well above  $c^*$  should be the same for cyclic and linear species, being the outcome of interactions of range shorter than molecular dimensions,<sup>7</sup> a scaling law in  $k(c/c^*)^m$  would predict different behaviors for cyclic and linear polymer. The discrepancy is not resolved by postulating different prefactors  $k$  since the ratio ( $c^*_{\text{cyclic}}/c^*_{\text{linear}}$ ) and also the power  $m$  depend on solvent quality. The concentration  $c^*$  is apparently included in the power law partly to fix the concentration where the law begins to apply and partly as an intuitively reasonable way to render the scaling argument dimensionless. The resulting discrepancy in predictions for molecules of linear and cyclic geometries leads to the surprising conclusion that  $c/c^*$  is not a universal reduced concentration.

In the plateau region, differences exist between the surface pressures from cyclic and linear PDMS. An analysis of the behavior of rings and chains in this region is reported elsewhere.<sup>21</sup>

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## References and Notes

- (1) G. L. Gaines, Jr., "Insoluble Monolayers at Liquid-Gas Interfaces", Interscience, New York, 1966.
- (2) D. J. Crisp, in "Surface Phenomena in Chemistry and Biology", J. F. Danielli, K. G. A. Pankhurst, and A. C. Riddiford, Eds., Pergamon Press, New York, 1958.
- (3) R. Vilanove and F. Rondelez, *Phys. Rev. Lett.*, **45**, 1502 (1980).
- (4) A. Takahashi, A. Yoshida, and M. Kawaguchi, *Macromolecules*, **15**, 1196 (1982).
- (5) M. Kawaguchi, A. Yoshida, and A. Takahashi, *Macromolecules*, **16**, 956 (1983).
- (6) M. Daoud and G. Jannink, *J. Phys. (Paris)*, **37**, 973 (1976).
- (7) P.-G. de Gennes, "Scaling Concepts in Polymer Physics", Cornell University Press, Ithaca, NY, 1979.
- (8) I. Majid, Z. V. Djordjevic, and H. E. Stanley, *Phys. Rev. Lett.*, **51**, 1282 (1983); B. Nienhuis, *Phys. Rev. Lett.*, **49**, 1062 (1982); J. C. Le Guillou and J. Zinn-Justin, *Phys. Rev. Lett.*, **39**, 95 (1977).
- (9) M. J. Stephen and J. L. McCauley, Jr., *Phys. Lett.*, **44A**, 89 (1973); J. Tobochnik, I. Webman, J. L. Lebowitz, and J. H. Kalos, *Macromolecules*, **15**, 549 (1982).
- (10) R. Ober and R. Vilanove, *Colloid Polym. Sci.*, **255**, 1067 (1977).
- (11) W. H. Banks, *Nature (London)*, **174**, 365 (1954).
- (12) A. H. Ellison and W. A. Zisman, *J. Phys. Chem.*, **60**, 416 (1956).
- (13) N. L. Jarvis, *J. Colloid Interface Sci.*, **29**, 647 (1969).
- (14) W. Fox, P. W. Taylor, and W. A. Zisman, *Ind. Eng. Chem.*, **59**, 1401 (1947).
- (15) M. J. Newing, *Trans. Faraday Soc.*, **46**, 755 (1950).
- (16) W. Noll, H. Steinbach, and Chr. Sucker, *Ber. Bunsenges. Phys. Chem.*, **67**, 407 (1963).
- (17) M. K. Bennett and W. A. Zisman, *Macromolecules*, **4**, 47 (1971).
- (18) K. Dodgson and J. A. Semlyen, *Polymer*, **18**, 1265 (1977).
- (19) K. Dodgson, D. Sympson, and J. A. Semlyen, *Polymer*, **19**, 1285 (1978).
- (20) J. A. Semlyen and P. V. Wright, in "Chromatography of Synthetic Polymers and Biopolymers", R. Epton, Ed., Ellis Horwood, Chichester, 1977.
- (21) S. Granick, S. J. Clarson, T. R. Formoy, and J. A. Semlyen, *Polymer*, in press.
- (22) K. Dodgson, D. J. Bannister, and J. A. Semlyen, *Polymer*, **21**, 663 (1980).
- (23) J. S. Higgins, K. Dodgson, and J. A. Semlyen, *Polymer*, **20**, 553 (1979).
- (24) J. S. Higgins, K. Ma, L. K. Nicholson, J. B. Hayter, K. Dodgson, and J. A. Semlyen, *Polymer*, **24**, 793 (1983).
- (25) C. J. C. Edwards, R. F. T. Stepto, and J. A. Semlyen, *Polymer*, **23**, 869 (1982).
- (26) C. J. C. Edwards, R. F. T. Stepto, and J. A. Semlyen, *Polymer*, **21**, 781 (1980).
- (27) C. J. C. Edwards, R. F. T. Stepto, and J. A. Semlyen, *Polymer*, **23**, 865 (1982).
- (28) C. J. C. Edwards, S. Bantle, W. Burchard, R. F. T. Stepto, and J. A. Semlyen, *Polymer*, **23**, 873 (1982).
- (29) L. Garrido, J. E. Mark, S. J. Clarson, and J. A. Semlyen, *Polymer*, in press.
- (30) D. J. Burton, R. K. Harris, K. Dodgson, C. J. Pellow, and J. A. Semlyen, *Polym. Commun.*, **24**, 278 (1983).
- (31) C. W. Macosko and G. S. Benjamin, *Pure Appl. Chem.*, **53**, 1505 (1983).
- (32) J. P. Munch, J. Herz, S. Boileau, and S. Candau, *Macromolecules*, **14**, 1370 (1981).
- (33) W. D. Harkins and H. F. Jordan, *J. Am. Chem. Soc.*, **52**, 1751 (1930).
- (34) T. Tompkins and R. E. Neuman, in preparation.
- (35) J. Guastalla, C. R. *Hebd. Séances Acad. Sci.*, **208**, 1078 (1939).
- (36) R. Defay and I. Prigogine, "Surface Tension and Adsorption", Wiley, New York, 1966.
- (37) F. Rondelez, personal communication.
- (38) P.-G. de Gennes, personal communication.
- (39) S. J. Singer, *J. Chem. Phys.*, **16**, 872 (1943).
- (40) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY, 1953.
- (41) L. Ter Minassian-Saraga and I. Prigogine, *Mem. Serv. Chim. Etat (Paris)*, **38**, 109 (1953).
- (42) K. Motomura and R. Matuura, *J. Colloid Sci.*, **18**, 52 (1963).
- (43) M. L. Huggins, *Makromol. Chem.*, **87**, 119 (1965); M. L. Huggins, *Kolloid Z. Z. Polym.*, **251**, 449 (1973).
- (44) H. L. Frisch and R. Simha, *J. Chem. Phys.*, **27**, 702 (1957).
- (45) J. Parker and J. L. Shereshfsky, *J. Phys. Chem.*, **58**, 850 (1954).
- (46) R. Ober and R. Vilanove, private communication.
- (47) R. L. Schuler and W. A. Zisman, *J. Phys. Chem.*, **74**, 1523 (1970).
- (48) D. J. Crisp, *J. Colloid Sci.*, **1**, 49 (1946).
- (49) K. Motomura, *J. Colloid Sci.*, **19**, 425 (1964).
- (50) J. J. Prentis, *J. Chem. Phys.*, **76**, 1574 (1982).
- (51) A. Baumgärtner, *J. Chem. Phys.*, **76**, 4275 (1982).
- (52) M. Kawaguchi, S. Komatsu, M. Matsuzumi, and A. Takahashi, *J. Colloid Interface Sci.*, **102**, 356 (1984).