

# Studies of cyclic and linear poly(dimethylsiloxanes): 18. Surface pressures of the monolayers in the plateau region

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Measurements of the two-dimensional surface pressure  $\pi$  have been made as a function of average area per monomer  $A$  at areas too small to support a single monolayer, for films of cyclic and linear poly(dimethylsiloxane) (PDMS) spread on the surface of water at temperatures between 6°C and 31°C. The number-average numbers of monomer units were 10 to 196 for the rings and 10 to  $1.2 \times 10^5$  for the linear chains. The surface pressures were stable with time for films formed from molecules with more than 20 monomer units. For these films, two plateaux of surface pressure linked by a rounded step were observed for both rings and chains, and the step occurred at the same average area per monomer. However, although the levels of the plateaux were the same for films formed from all linear species, increases in levels of the plateaux with decreasing number of monomer units were observed for cyclic species. The temperature coefficient of the surface pressure was negative in all instances, suggesting that surface entropy is gained upon compression. The unstable films formed from the linear and cyclic decamers were also studied. The former displayed a step in the plateau region, the latter did not appear to. The present findings suggest that cyclic and linear PDMS with more than 20 monomer units collapse by a common mechanism. If the long-standing hypothesis that PDMS collapses by adopting a helical configuration is correct, this implies that rings with as few as 20 repeat units on the average coil into helices.

**(Keywords: cyclic poly(dimethylsiloxane); linear poly(dimethylsiloxane); two-dimensional properties; monolayer; surface pressure; plateau region)**

## INTRODUCTION

The preparation and physical investigation of sharp fractions of cyclic poly(dimethylsiloxane) (PDMS) have been described in previous papers in this series<sup>1-15</sup>. Molecules with number-average degrees of polymerization up to 500 have been prepared, in quantities up to several grams. Their simple ring structures have been confirmed by dilute solution<sup>1</sup> and bulk<sup>4</sup> viscometry, small-angle neutron scattering<sup>3</sup>, photon correlation spectroscopy<sup>8</sup>, diffusion measurements<sup>5,7,9,12,15</sup>, and <sup>29</sup>Si nuclear magnetic resonance spectroscopy<sup>16</sup>. Linear fractions have also been investigated by these techniques for purposes of comparison.

In this paper, we extend these comparisons to the properties of monomolecular films of PDMS. For many years it has been known<sup>17</sup> that when linear PDMS is spread at the water-air interface, a surface pressure develops that is analogous to the osmotic pressure characteristic of a three-dimensional solution. The dependence of surface pressure on surface concentration is simpler than that observed for many small

molecules<sup>18,19</sup>. Three regions can be qualitatively distinguished. In the dilute region of surface coverage, 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 higher surface coverages a transition region follows. Here the surface pressure rises much more rapidly than proportional to the surface concentration and is independent of molecular weight. In this region, the surface pressures of cyclic and linear PDMS are indistinguishable<sup>20</sup>. At surface concentrations that correspond approximately to full coverage of the surface by polymer, there begins a plateau of relatively constant surface pressure. It is generally agreed that the plateau reflects collapse of the monolayer to a three-dimensional state. Comparison of the surface pressures of cyclic and linear PDMS in the plateau region is the subject of the present study.

## EXPERIMENTAL

### Materials

Fractions of linear poly(dimethylsiloxanes)  $(\text{CH}_3)_3\text{SiO}[(\text{CH}_3)_2\text{SiO}]_y\text{Si}(\text{CH}_3)_3$  and cyclic poly-

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(dimethylsiloxanes)  $[(\text{CH}_3)_2\text{SiO}]_x$  were obtained at the University of York by methods described previously<sup>1,2,21</sup>. The linear fractions, which were methyl-terminated, were obtained by fractional distillation (polymers L1 and L2) or by preparative gel permeation chromatography (g.p.c.) (polymers L3–L5), starting from Dow Corning dimethicones. The cyclic fractions were recovered from ring-chain equilibration reactions in toluene at 110°C, before being separated into fractions by vacuum fractional distillation (polymers R1 and R2) and by preparative g.p.c. (polymers R3–R5). Number-average molecular weights  $M_n$ , number-average degrees of polymerization  $\bar{x}_n$  and  $\bar{y}_n$ , and ratios  $M_w/M_n$  of weight-average to number-average molecular weight are listed in Table 1.

Care was taken throughout to avoid contamination. The fractions obtained by fractional distillation were used without further purification. The fractions obtained by preparative g.p.c. were washed several times with methanol; dissolved in toluene; filtered using 0.45  $\mu\text{m}$  filters (Millipore Ltd.); precipitated from toluene using methanol as the non-solvent; and dried by rotary evaporation and by placing the samples in a vacuum oven at 60°C for 24 h.

An additional sample of extremely high molecular weight methyl-terminated linear PDMS, polymer L6 in Table 1, was generously donated by Dr S. Boileau of the Collège de France and Professor C. W. Macosko of the University of Minnesota.

#### Surface pressure measurements

Experiments were carried out at the Collège de France in a thermostatically controlled Teflon-coated trough provided with a Lauda film balance. The Wilhelmy plate method of measurement was generally used, using a platinum plate 2 cm long suspended from a sensitive LVDT transducer (HBM Model Q11). Isolated direct measurements of the surface pressure were also made by the Langmuir method to verify that the two methods gave indistinguishable results. With the Wilhelmy method, the surface pressure was determined with a precision of 0.1  $\text{mN m}^{-1}$ . Spectroscopic grade (Merck) hexane and chloroform were used as spreading solvents. The water was triply-distilled. The water temperature was controlled to 0.1°C.

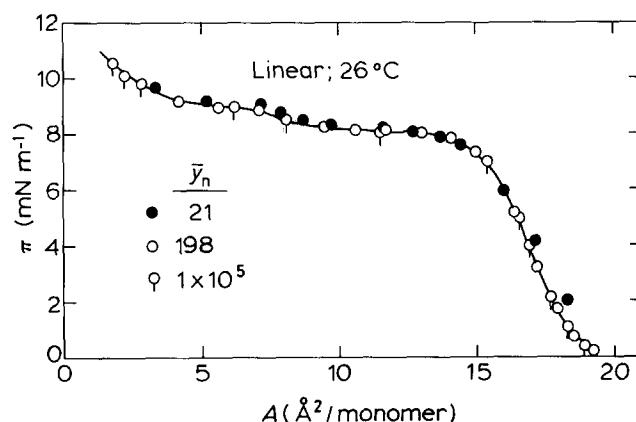
The surface concentration of polymer was varied by

**Table 1** Characterization of the linear and cyclic PDMS

Fraction	$\bar{y}_n$ and $\bar{x}_n$ (to nearest integer)	$M_n$	$M_w/M_n$
Linear PDMS $(\text{CH}_3)_3\text{SiO}[(\text{CH}_3)_2\text{SiO}]_y\text{Si}(\text{CH}_3)_3$			
L1	10	890	1.01
L2	21	1670	1.01
L3	83	6330	1.17
L4	134	10060	1.15
L5	198	14800	1.11
L6	$1.2 \times 10^5$	$9 \times 10^6$ <sup>b</sup>	<1.2 <sup>a</sup>
Cyclic PDMS $[(\text{CH}_3)_2\text{SiO}]_x$			
R1	10	730	1.07
R2	20	1480	1.02
R3	73	5430	1.03
R4	122	9030	1.05
R5	196	14500	1.03

<sup>a</sup> Measured<sup>22</sup> for similar samples

<sup>b</sup> Calculated from  $M_w$  measured<sup>23</sup> by light scattering



**Figure 1** Surface pressure at 26°C of water bearing linear PDMS of several degrees of polymerization as indicated, plotted against surface area per monomer

successive compressions. The measurements were quantitatively reversible over the entire concentration range<sup>20</sup>. Typically the surface was compressed by a factor of 14, starting from an initial area of 0.08  $\text{m}^2$ . It was verified that the measurements did not depend on the quantity of polymer deposited<sup>20</sup>. Spreading of polymer on the liquid surfaces was carried out by applying 2 to 6  $\mu\text{l}$  solutions of the polymer in the spreading solvents (0.05 to 0.5  $\text{mg ml}^{-1}$ ) using an Agla microsyringe driven by a micrometer head. It was 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  $\text{mN m}^{-1}$  at maximum compression.

## RESULTS

#### Measurements at 26°C

Figure 1 shows that in the plateau region, the pressure–area diagrams of the linear fractions were indistinguishable. Surface pressure is plotted in the conventional fashion, against average surface area per monomer. Here and in the other pressure–area diagrams, only representative points are shown for clarity. At all areas, the surface pressure equilibrated within a few seconds of changing the surface area and did not diminish with time. In Figure 1, fractions ranging from  $\bar{y}_n=21$  to  $1 \times 10^5$  display the same pattern of variation of surface pressure with decreasing area per monomer. The straight-line portion of the transition zone extrapolates to zero pressure at 18.8  $\text{Å}^2/\text{monomer}$ , in good agreement with the value  $19.3 \pm 1.3 \text{ Å}^2/\text{monomer}$  found by Noll and coworkers<sup>24</sup>. At lesser surface areas a primary plateau follows. It is difficult to define the exact onset of the plateau, since curvature in the plateau region depends on the temperature of measurement (see Figure 3). However, at all temperatures the knee between the transition and plateau zones is tangent to a line of slope  $-1$  at 15.5  $\text{Å}^2/\text{monomer}$ . A rounded step to a secondary plateau occurs at 7–9  $\text{Å}^2/\text{monomer}$ . This is tangent to a line of slope  $-1$  at 7.8  $\text{Å}^2/\text{monomer}$ . Finally, at areas less than 4  $\text{Å}^2/\text{monomer}$ , there commences a slow, featureless rise in surface pressure.

Linear polymer L1 ( $\bar{y}_n=10$ ) also exhibited this general pattern, but quantitative measurements were not possible owing to a loss of film pressure with time. This has been

observed previously for small oligomers and has been attributed to volatility or solubility of the oligomers in the water substrate<sup>24</sup>.

Findings for the cyclic polymers are shown in Figure 2. Surface pressure is plotted against average surface area per monomer, and findings for the linear species are included for comparison. The qualitative pattern in the plateau region is similar to that for the linear species, but the levels and curvatures of the plateaux, and the magnitude of the step, increase with decreasing molecular size. The areas where the curves are tangent to lines of slope  $-1$  are the same as for the linear species. Table 2 tabulates the levels  $\pi_1$  and  $\pi_2$  of the plateau regions (gauged as the surface pressures at 9.0 and 7.0  $\text{\AA}^2/\text{monomer}$ , respectively) and the sizes  $\Delta\pi$  of the steps. All the cyclic species have plateau levels slightly higher than the  $\pi_1=8.3$  and  $\pi_2=8.9$   $\text{mN m}^{-1}$  characteristic of the linear polymers. A plot of  $\pi_1$  versus  $\bar{x}_n$  would be an apparent straight line with negative slope. But  $\Delta\pi$  is much larger for  $\bar{x}_n=20$  than extrapolation of the points for the larger cyclics would indicate.

In view of the upturn in  $\Delta\pi$  for  $\bar{x}_n=20$ , it is interesting that the cyclic species with  $\bar{x}_n=10$  appears to possess no step at all. Quantitative pressure-area curves could not be obtained for this oligomer owing to a loss of film pressure with time. The rate of surface pressure decay at 7  $\text{mN m}^{-1}$  was a factor of 0.002 per min. Neither rapid compression measurements in the plateau region (indicated by the dashed line in Figure 3), nor monitoring the surface pressure decay following deposition of a large quantity of polymer, suggested the presence of a step for sample R1.

#### Effect of temperature

The effect of temperature on the film pressures of linear

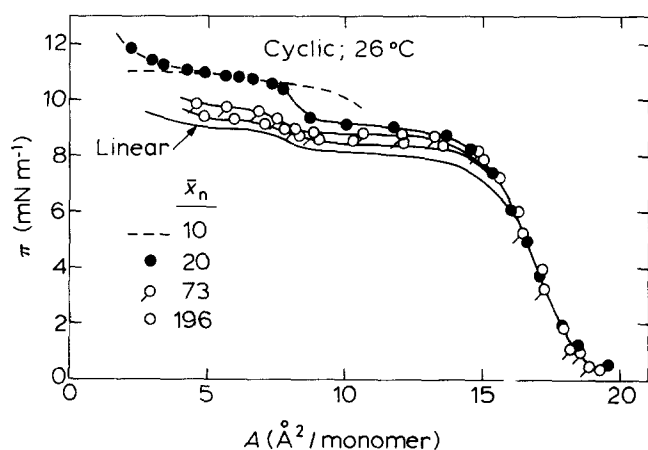


Figure 2 Surface pressure at 26°C of water bearing cyclic PDMS of several degrees of polymerization as indicated, plotted against surface area per monomer

Table 2 Dependence of plateau pressures of cyclic PDMS on degree of polymerization; 26°C

$\bar{x}_n$	$\pi_1^a$ ( $\text{mN m}^{-1}$ )	$\pi_2^b$ ( $\text{mN m}^{-1}$ )	$\Delta\pi$ ( $\text{mN m}^{-1}$ )
20	9.3	10.7	1.4
73	8.8	9.6	0.8
122	8.6	9.3	0.7
196	8.6	9.2	0.6

<sup>a</sup> Measured at 9.0  $\text{\AA}^2/\text{monomer}$

<sup>b</sup> Measured at 7.0  $\text{\AA}^2/\text{monomer}$

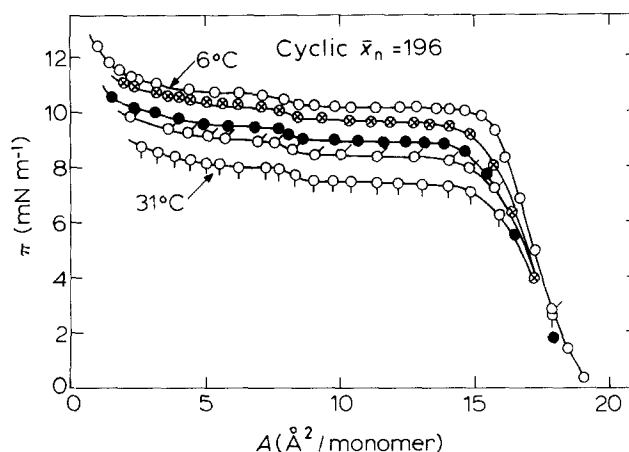


Figure 3 Surface pressure of water bearing cyclic polymer R5, plotted against surface area per monomer. Points: (○), 6°C; (⊗), 11°C; (●), 18°C; (○), 26°C; (○), 31°C

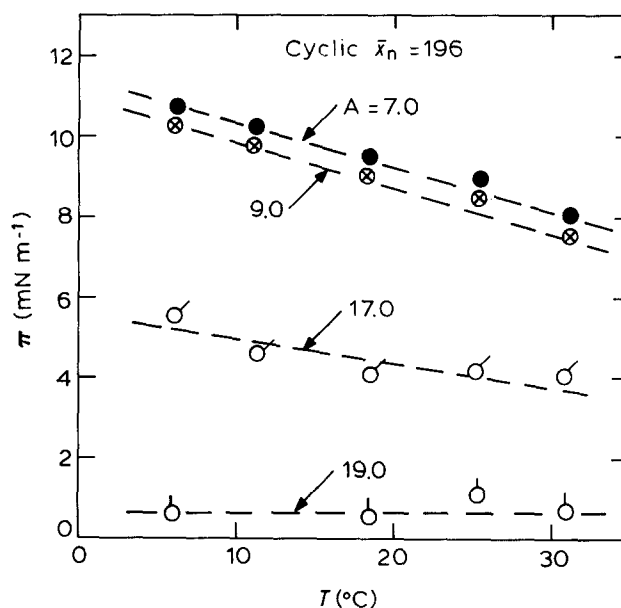


Figure 4 Surface pressure of water bearing cyclic polymer R5, measured at four areas per monomer as indicated, plotted against temperature

and cyclic PDMS was also studied. Figure 3 shows pressure-area diagrams of cyclic polymer R5 ( $\bar{x}_n=196$ ) at four temperatures between 6°C and 31°C. Whereas the curves merge in the transition region, the plateau levels are higher at lower temperatures. At 6°C the level of the first plateau is a factor of 1.35 higher than it is at 31°C and also is flatter. However, the size of the step and the area where the curves are tangent to lines of slope  $-1$  do not change over this temperature range. The same was found of the other cyclic and linear species whose film pressures were stable. These findings, except for the fixed position of the step, are in general agreement with the pioneering experiments of Zisman and coworkers<sup>17</sup> for linear PDMS.

In Figure 4, the data in Figure 3 are compared more closely. Surface pressures of cyclic polymer R5 are plotted against temperature at four values of area per monomer. In the two plateau regions (at 7.0 and 9.0  $\text{\AA}^2/\text{monomer}$ ), the slope  $d\pi/dT$  is negative, approximately  $-0.1$   $\text{mN m}^{-1}$  per degree at both areas. At a surface area corresponding to the middle of the transition zone (17.0  $\text{\AA}^2/\text{monomer}$ ),  $d\pi/dT$  is less negative, approximately  $-0.05$   $\text{mN m}^{-1}$  per

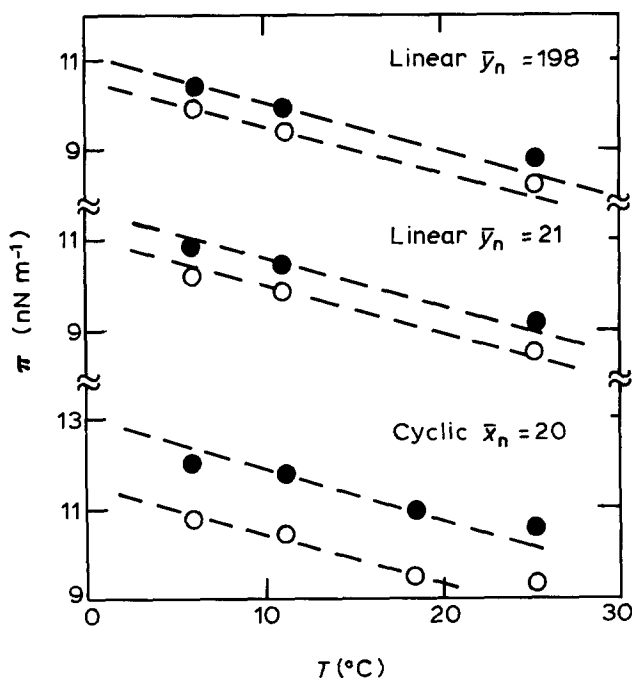
degree. Near the onset of the transition zone ( $19.0 \text{ \AA}^2/\text{monomer}$ ),  $d\pi/dT=0$  within experimental error.

Other cyclic and linear polymers followed the same pattern in both the plateau and transition regions. At each temperature, the levels of the plateaux of the cyclic species increased with decreasing degree of polymerization, while the pressure–area diagrams of the linear species were indistinguishable. In *Figure 5*, surface pressures at  $9.0$  and  $7.0 \text{ \AA}^2/\text{monomer}$  are plotted against temperature for polymers R2 ( $\bar{x}_n = 20$ ), L2 ( $\bar{y}_n = 21$ ) and L5 ( $\bar{y}_n = 198$ ). Lines through the points are drawn with the same slope as for polymer R5 at these areas. It is evident that for cyclic and linear species of widely different degrees of polymerization, the slope  $d\pi/dT$  is negative. The numerical values of the slopes appear to be the same within experimental error.

## DISCUSSION

The aim of the present experiments was to compare the surface properties of cyclic and linear PDMS in the plateau region. Film pressures were found to be stable with time for films formed from molecules with more than 20 monomer units. For these films two plateaux of surface pressure linked by a rounded step were observed for both rings and chains, and the step occurred at the same average area per monomer. However, although the levels of the plateaux were the same for films formed from all linear species, increases in the levels of the plateaux with decreasing degree of polymerization were observed for the cyclic species. The temperature coefficient of the surface pressure was negative in all instances. To the best of our knowledge, surface pressures of cyclic PDMS in the plateau region, and of linear PDMS of such a wide range of molecular weight, have not been reported previously.

As pointed out long ago by Crisp<sup>19</sup>, observation that



**Figure 5** Surface pressure  $\pi$  of water bearing cyclic and linear PDMS as indicated, plotted against temperature. Points: (○),  $\pi$  measured at  $9.0 \text{ \AA}^2/\text{monomer}$ ; (●),  $\pi$  measured at  $7.0 \text{ \AA}^2/\text{monomer}$ . Lines through the points are drawn with the same slope as for  $\pi$  measured at these areas for polymer R5 in *Figure 4*

the temperature coefficient of the surface pressure is negative suggests that the surface entropy of PDMS films increases with decreasing surface area. This follows from the thermodynamic relation

$$\pi = -\left(\frac{\partial G}{\partial A}\right)_{N_2, T} = -\left(\frac{\partial H}{\partial A}\right)_{N_2, T} + T\left(\frac{\partial S}{\partial A}\right)_{N_2, T} \quad (1)$$

Here  $G$  is the surface Gibbs free energy,  $H$  the surface enthalpy,  $S$  the surface entropy,  $A$  the area,  $N_2$  the number of adsorbed molecules, and  $T$  the absolute temperature. Over a narrow temperature range, it is reasonable to consider the partial derivatives in equation (1) to be independent of temperature, so that

$$\left(\frac{\partial \pi}{\partial T}\right)_{N_2} \approx \left(\frac{\partial S}{\partial A}\right)_{N_2} \quad (2)$$

To the extent that this is correct, it implies that in the present experiments, the surface entropy in the plateau region is higher than in the transition region.

We are not aware of a molecular theory capable of explaining the present pressure–area diagrams quantitatively. In a paper published in 1947, Zisman and coworkers<sup>17</sup> proposed a model for the mechanism of collapse of linear PDMS, which has been reiterated many times over the years<sup>24–29</sup>. The presumption is that features in the pressure–area diagram parallel changes in molecular conformation. At areas corresponding to the knee between the transition and plateau regions, a closepacked array of siloxane units is pictured to cover the water surface. Levelling of surface pressure upon compression to areas too small to support a monolayer is taken to reflect progressive coiling of the residues into helices oriented parallel to the surface. The step in surface pressure then occurs after the surface is completely covered with helices, as the helices tend to be pushed upright. Molecular models of helices with six residues per repeat unit correctly predict the step to occur at  $7\text{--}8 \text{ \AA}^2/\text{monomer}$ <sup>17,24–29</sup>. The model has also been interpreted to be consistent with measurements of damping of capillary waves<sup>28</sup> and measurement of surface potential and dipole moment<sup>29</sup>.

If linear PDMS collapses by coiling into a helical conformation, then it would seem that sufficiently small rings must collapse by a different mechanism. In the present experiments, all the stable films of rings displayed the same pattern of pressure–area variation as did those of linear molecules, implying that cyclic and linear PDMS with more than 20 monomer units collapse by a common mechanism. Experiments on rings and chains of smaller average size were complicated by instability of the film pressures. Thus the present experiments do not appear to provide conclusive evidence for or against the Zisman model. An alternative interpretation of the mechanism of collapse, based on these and other measurements, will be presented elsewhere.

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