

- (8) Shibayama, M.; Hashimoto, T.; Kawai, H. *Macromolecules* 1983, 16, 1434 and cognate references.
- (9) Richards, R. W.; Thomason, J. L. *Polymer* 1981, 22, 581.
- (10) Richards, R. W.; Thomason, J. L. *Macromolecules* 1983, 16, 982.
- (11) Richards, R. W.; Thomason, J. L. *Polymer* 1983, 24, 1089.
- (12) Berney, C. V.; Cohen, R. E.; Bates, F. S. *Polymer* 1982, 23, 1222.
- (13) Bates, F. S.; Cohen, R. E.; Berney, C. V. *Macromolecules* 1982, 15, 589.
- (14) Bates, F. S.; Berney, C. V.; Cohen, R. E. *Macromolecules* 1983, 16, 1101.
- (15) Rayleigh, Lord. *Proc. R. Soc. London, Ser. A* 1914, 90, 219.
- (16) Fournet, G. *Bull. Soc. Franc. Mineral. Cristallogr.* 1951, 74, 39.
- (17) Schelten, J.; Schmatz, W. J. *Appl. Crystallogr.* 1980, 13, 385.
- (18) Goyal, P. S.; King, J. S.; Summerfield, G. C. *Polymer* 1983, 24, 131.
- (19) Ruland, W. "Colloque Franco-Américain sur la Diffusion des Rayons-X et des Neutrons aux Petits Angles par les Polymères", Strasbourg, 1980.
- (20) Ghosh, R. E. "A Computing Guide for Small Angle Scattering Experiments"; Institut Laue-Langevin: Grenoble, 1981; Report No. 81GH29T.
- (21) Guinier, A.; Fournet, G. "Small Angle Scattering of X-Rays"; Wiley: New York, 1955.
- (22) Porod, G. In "Small Angle X-ray Scattering"; Glatter, O., Kratky, O., Eds.; Academic Press: London, 1982; Chapter 2.
- (23) Zernicke, F.; Prins, J. A. Z. *Phys.* 1927, 41, 184.
- (24) Yarusso, D. J.; Cooper, S. L. *Macromolecules* 1983, 16, 1871.
- (25) McIntyre, D.; Campus-Lopez, E. *Macromolecules* 1970, 3, 322.
- (26) Schultz, J. M. "Diffraction for Materials Scientists"; Prentice-Hall: Englewood Cliffs, NJ, 1982.
- (27) Cullity, B. E. "Elements of X-Ray Diffraction", 2nd ed.; Addison-Wesley: Reading, MA, 1978.
- (28) Brown, B. L.; Taylor, T. J. *Appl. Polym. Sci.* 1974, 18, 1385.
- (29) Vainshtein, B. K. "Diffraction of X-Rays by Chain Molecules"; Elsevier: Amsterdam, 1966.
- (30) Hosemann, R.; Bagchi, S. N. "Direct Analysis of Diffraction by Matter"; North-Holland: Amsterdam, 1962.
- (31) Vonck, C. G. In "Small Angle X-Ray Scattering"; Glatter, O., Kratky, O., Eds.; Academic Press: London, 1982; Chapter 13.
- (32) Harrison, I. R.; Kozmiski, S. J.; Varnell, W. D.; Wang, J. I. J. *Polym. Sci., Polym. Phys. Ed.* 1981, 19, 487.
- (33) Strobl, G. R.; Schneider, M. J. *Polym. Sci., Polym. Phys. Ed.* 1980, 18, 1343.
- (34) Source listings of programs may be obtained from the authors.

Surface Pressure from Block Copolymers with One Block Forming a Monolayer and the Other Block Dangling in Solution[†]

Steve Granick*

Physique de la Matière Condensée, § Collège de France, 75231 Paris Cedex 05, France

Jean Herz

*Centre de Recherches sur les Macromolécules (C.N.R.S.), 67083 Strasbourg Cedex, France.
Received April 23, 1984*

ABSTRACT: Surface pressure has been measured as a function of surface concentration for monolayers of poly(dimethylsiloxane)-polystyrene (PDMS-PS) diblock copolymers, PDMS-poly(α -methylstyrene) (PDMS-P α MS) multiblock copolymers, and the respective homopolymers, spread on the surface against air of tricresyl phosphate at 26 °C. A sparingly soluble monolayer was formed by PDMS homopolymer. No surface pressure was associated with either PS or P α MS homopolymer; these appeared to pass into bulk solution. For the block copolymers, at low surface concentrations the surface pressure was indistinguishable from that for PDMS homopolymer at the same concentration of PDMS. At higher concentrations the surface pressure exceeded this value, to an extent which increased with increasing surface concentration of PS or P α MS. The supplemental surface pressure from dangling chains was calculated by subtraction. The findings are in qualitative agreement with theoretical predictions by de Gennes, Alexander, and Cantor that osmotic interactions between polymer chains dangling into a liquid from an interface contribute substantially to the reduction of surface tension. Idealizations in the theoretical models are noted.

Introduction

Block copolymers are amphiphilic and can behave as surfactants. At small concentrations in a liquid they can concentrate at the surface, lowering the surface tension considerably.¹ This property finds technological applications in blends of immiscible polymeric liquids.² At higher concentrations, block copolymers can assemble into micelles³ or other organized structures.⁴ They can bring into solution material that is otherwise insoluble.⁵ The outlook for understanding this behavior appears in some respects more favorable for uncharged amorphous block copolymers than for surfactants of the traditional type.⁶

The absence of charges simplifies the situation compared to that for surfactants with polar heads. And in contrast to small nonionic surfactants, the long length of flexible polymers makes possible predictions based on the statistical thermodynamics of homopolymer solutions, which is relatively well understood. Study of block copolymers for the elucidation of surfactant action has been urged.⁶⁻⁹

A theory for the interaction between polymer chains dangling from one end into a liquid has been proposed by de Gennes,⁶ Alexander,⁷ and Cantor.⁸ A parallel can be drawn between the dangling chains and the tails of conventional small amphiphilic molecules. In the theoretical models, at a water-oil interface a hydrophilic and a hydrophobic block straddle the interface, each dangling into the liquid for which it has affinity; at a liquid-air interface one of the blocks adsorbs tightly, riding on the surface as a buoy which traps the other. In both cases there is considered to exist a well-defined surface phase of polymer in thin three-dimensional solution, but attached to the

[†] We take pleasure in dedicating this paper to Pierre Thirion on the occasion of his retirement.

* To whom correspondence may be addressed at Polymer Group and Department of Ceramic Engineering, University of Illinois, Urbana, IL 61801.

[‡] Equipe de recherche associé au C.N.R.S.

interface, whose thermodynamics can be analyzed in a manner similar to that for a macroscopic polymer network swollen with solvent. The key prediction is that osmotic interactions between dangling chains can reduce the surface tension considerably. The amount by which the surface tension is reduced from that of the pure liquid is the surface pressure.

This paper reports experimental findings for block copolymers with configurations close to those postulated theoretically. These configurations were more difficult to achieve experimentally than might be expected. They were achieved at the surface against air of tricresyl phosphate: here poly(dimethylsiloxane) (PDMS) forms a sparingly soluble monolayer,^{10,11} while polystyrene (PS) and poly(α -methylstyrene) (P α MS) spread at the surface appear to go into bulk solution. Tricresyl phosphate is known to be a better than Θ solvent for PS.¹²

Theory

The Gibbs free energy ΔG of an assembly of polymer chains attached to a liquid interface, each dangling an average distance L into an adjoining liquid to form a surface phase with polymer volume fraction ϕ_2 sufficiently high that dangling chains overlap, has been described by de Gennes⁶ and Cantor.⁸

$$\Delta G/kT = 3n_2L^2/2L_0^2 + n_1 \ln(1 - \phi_2) + \chi n_1\phi_2 \quad (1)$$

Assumptions contained in eq 1 are discussed in the Conclusions section. The last two terms on the right are the Flory-Huggins²⁷ osmotic free energy of mixing for polymers attached to the surface. This tends to promote low polymer concentration by stretching the chains. The first term is the Gaussian elastic free energy of stretching. The numbers of solvent and polymer molecules are n_1 and n_2 , respectively; the average chain end-to-end distance is L_0 at infinite dilution and L otherwise; χ is the Flory-Huggins²⁷ polymer-solvent interaction parameter, k the Boltzmann constant, and T the absolute temperature. The linear dimension a of a lattice site is the same for monomers and solvent molecules (the case if these dimensions are different is treated by Cantor⁸) and N is the number of monomers per polymer chain. Equation 1 depends on the system's interfacial area A by the identity $\phi_2 = n_2Na^3/AL$.

The surface pressure $\pi = -(\partial\Delta G/\partial A)_{n_2,T,P}$ is determined once the average chain dimension L has been specified by minimizing the surface phase's free energy with respect to L . For this calculation it is convenient to expand eq 1 in powers of ϕ_2 . For chains present at small concentrations in a liquid of better than Θ solvent quality, terms in ϕ_2^3 and higher may be neglected, and the results are

$$L \propto N^{2/3}c^{1/3}(1/2 - \chi)^{1/2} \quad (2)$$

$$\pi \propto N^{-2/3}c^{5/3}(1/2 - \chi)^{2/3} \quad (3)$$

Here the approximation $L_0^2 = Na^2$ is made for convenience and the total area A has been expressed as surface mass concentration $c = w/A$, where w is the mass of dangling chains. For the semidilute region of volume fractions (coil overlap accompanied by low overall polymer concentration), Alexander⁷ has obtained a similar prediction, $\pi \propto c^{11/6}$ for polymers of high molecular weight, from scaling arguments.

At higher concentrations or in a poor solvent, terms of higher order make important contributions to the free energy. However, the power-law dependencies on degree of polymerization N and surface concentration c are at first not vastly different. If the term proportional to ϕ_2^3 in the expansion of eq 1 were to dominate, $\pi \propto N^{-1}c^2$; if the term

Table I
Characterization of the Copolymers

code ^a	M_n		copolymer
	PDMS block	PS or P α MS block ^b	
Diblock Copolymer			
0.71	13 800	33 400	47 200
0.76	13 700	43 600	57 300
Multiblock Copolymer			
0.14	25 000	4 100	80 000
0.24	13 200	4 100	60 000
0.39	6 400	4 100	30 000
0.66	2 150	4 100	20 000

^a Also weight fraction PS or P α MS. ^b PS for diblock copolymers, P α MS for multiblock copolymers.

proportional to ϕ_2^4 were to dominate, $\pi \propto N^{-4/3}c^{7/3}$; and so forth. The actual surface pressure would of course include contributions from all these terms.

Experimental Section

Materials. Two families of block copolymers were studied. Two diblock copolymers of poly(dimethylsiloxane) (PDMS) and polystyrene (PS), prepared¹³ by anionic polymerization, were generously donated by Professor J. V. Dawkins of the Loughborough University of Technology. The number-average molecular weights M_n of the copolymers and of each of the copolymer blocks are listed in Table I. The ratios M_w/M_n of weight-average to number-average molecular weight were less than 1.25. In addition, a family of multiblock copolymers consisting of alternating units of PDMS and poly(α -methylstyrene) (P α MS) were prepared at the Centre de Recherches sur les Macromolécules with the kind assistance of Dr. Philippe Chaumont. The number-average molecular weights M_n of the copolymers and of each of the copolymer blocks are included in Table I. The synthesis by condensation of oligomers has been described previously.¹⁴ The terminal blocks were either PDMS or P α MS, at random. Although M_w/M_n was typically 3 for the copolymers, for the PDMS blocks it was typically 1.5 and for the P α MS blocks 1.1. In Table I, each copolymer is identified according to its weight fraction of PS or P α MS.

Two samples of linear PDMS homopolymer, polymers C and D in ref 11, were generously donated by Dr. J. A. Semlyen of the University of York. They had $M_n = 6300$ and 14800, and their ratios M_w/M_n were less than 1.2. Additional samples of PDMS homopolymer, generously donated by Dr. C. Millet and Dr. G. Soula of Rhône-Poulenc Recherches, were used in exploratory experiments. Samples of PS and P α MS homopolymers had $M_n = 17500$ and 4100, respectively, with $M_w/M_n = 1.1$.

For the monolayer studies, tricresyl phosphate (Fluka), a mixture of isomers used as received, was the liquid support. Its surface tension at 26 °C, measured by the de Nöuy ring method using the corrections of Harkins and Jordan,¹⁵ was 37.71 dyn/cm.

Methods. The apparatus and detailed methods are described elsewhere.¹¹ The monolayer experiments were carried out at the Collège de France, at 26 °C in a thermostated Teflon trough. The surface pressure was usually measured by the Wilhelmy method, using a sandblasted platinum plate 2 cm long. Previous experiments¹¹ have shown that direct measurement by the Langmuir method gave the same results for PDMS homopolymer spread on tricresyl phosphate and consequently that the contact angle of tricresyl phosphate was zero on the Wilhelmy plate. For the PDMS homopolymers, 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; discrepancies are ascribed to changes in the zero described below. For the block copolymer monolayers, additional uncertainty in the surface pressure owing to partial dissolution of the polymers at high surface concentrations is described below.

The polymers were spread from chloroform or benzene solutions at concentrations between 0.05 and 0.5 mg/mL. The spreading solvents were spectroscopic grade (Merck) and were used as received. The surface concentration was almost always varied by successive compression. Probably because of slow diffusion on

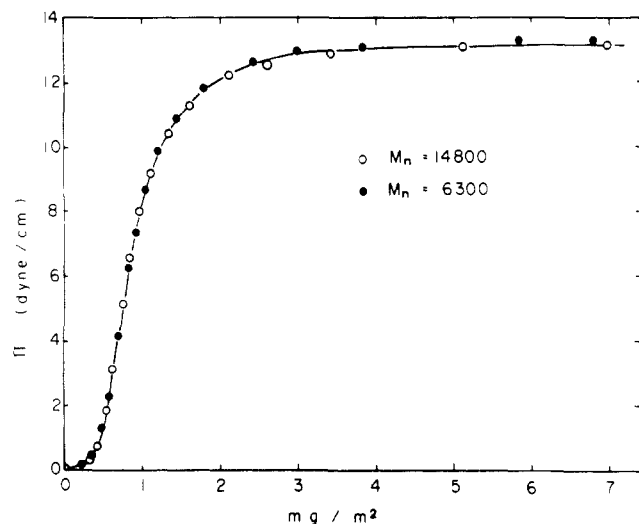


Figure 1. Surface pressure at 26 °C of tricresyl phosphate bearing PDMS of number-average molecular weights 6300 and 14 800, plotted against surface concentration of polymer.

the surface, the equilibration time was as long as 15 min for PDMS homopolymers when the surface pressure was low, and as long as 1 h for the copolymers, but not more than 2 min even for the copolymers when the surface pressure exceeded 2 dyn/cm. The rate of deposition onto the liquid surface did not affect the results except for the diblock copolymers, as described below. 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 0.3 dyn/cm at maximum compression.

Tricresyl phosphate tended to climb the platinum plate by capillary action, increasing the weight of the plate and generating spurious surface tension. To avoid this as much as possible, 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.

Results

Homopolymers. When tricresyl phosphate surfaces upon which PS or PDMS homopolymers had been spread were compressed, no surface pressure could be detected by either the Wilhelmy or Langmuir method, even upon compression to nominal polymer surface concentration corresponding to over 50 times full surface coverage. The polymers apparently passed into bulk solution.

That PDMS forms a sparingly soluble monolayer on tricresyl phosphate has been shown previously.^{10,11} In Figure 1, the surface pressure π is plotted against surface concentration of polymer for PDMS homopolymer of two molecular weights. The reproducibility of measurements, and the property that except at dilute concentrations the surface pressure associated with a linear polymer is independent of the polymer molecular weight,¹⁶ are illustrated. Consideration of molecular models^{17,18} shows that full monolayer coverage of the surface corresponds to a concentration somewhat under 1 mg/m². At concentrations less than this the transition zone occurs; here the surface pressure rises much faster than proportional to the surface concentration of polymer. The plateau zone follows at higher concentrations: this is usually interpreted^{16,19} as collapse of the polymer to a three-dimensional state. That the plot is so featureless in the plateau zone up to surface concentrations exceeding seven full monolayers is in contrast to the situation for PDMS spread on water²⁰ and suggests that on tricresyl phosphate well-defined multilayers do not form. PDMS probably collapses into tricresyl phosphate rather than into the air.

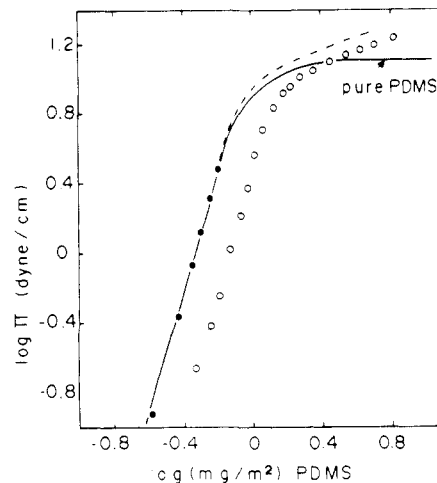


Figure 2. Surface pressure at 26 °C of tricresyl phosphate bearing PDMS homopolymer (solid line) and PDMS-PS diblock copolymer 0.76, plotted logarithmically against surface concentration of PDMS. Points: open circles, copolymer spread dropwise over 10 min; filled circles, copolymer spread dropwise over 2 h. Dashed line: curve for quick deposition shifted to pass through filled circles.

Previous experiments have shown that measurements of the surface pressure of PDMS are quantitatively reversible on the experimental time scale of 2 h in the transition zone up to the inflection point.¹¹ Experiments past the transition zone were also quantitatively reversible, but some irreversibility (on the order of 0.5 dyn/cm) appeared followed expansion back to 5 dyn/cm. This is believed to reflect in part the slow kinetics with which collapsed PDMS adsorbs back to a monolayer state.

PDMS-PS Copolymers. Figure 2 shows typical results. The surface pressure π is plotted logarithmically against the surface concentration of PDMS moieties, and results from Figure 1 for PDMS homopolymers are included for comparison. The open circles represent an experiment after copolymer 0.76 was spread at a normal rate, over the space of 10 min. The logarithmic slope in the transition zone is the same as for PDMS homopolymer, but the points are displaced to higher apparent surface concentrations of PDMS. When the copolymers were spread over the space of 30 min (not shown), the displacement on the logarithmic concentration scale was less, but the logarithmic slope the same. The discrepancy in concentrations disappeared completely when the copolymer was spread sufficiently slowly. The filled circles in Figure 2 represent an experiment after copolymer 0.76 was spread over a space of 2 h to a PDMS surface concentration before compression of only 0.1 mg/m². These results are quantitatively indistinguishable, over a 25-fold span of surface pressure, from those for PDMS homopolymer. As shown in Figure 4, the same was found for another family of block copolymers, for which the data did not depend on the rate of spreading. In Figure 2, the dotted line reproduces a smoothed curve through the open circles, but shifted 0.20 logarithmic units to lower surface concentrations. Although in the transition zone the surface pressure is indistinguishable from that attributable to the PDMS, beyond the transition zone the surface pressure is higher than can be explained in this way.

It appears likely that upon spreading at a normal rate, substantial quantities of the PDMS-PS copolymers dissolved before local copolymer concentrations on the surface could equalize by surface diffusion. The relatively long times needed for surface pressure to stabilize after surface area was changed have been noted already. Moreover,

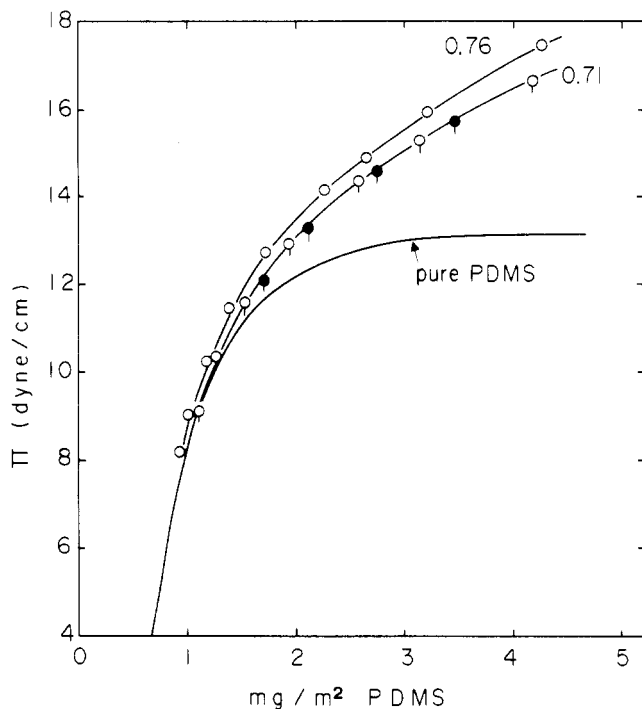


Figure 3. Surface pressure at 26 °C of tricresyl phosphate bearing PDMS homopolymer (solid line) and PDMS-PS diblock copolymers, plotted against surface concentration of PDMS. Fractional PS composition of copolymers is indicated in the figure. Reversibility of measurements for copolymer 0.71 is illustrated by comparison of measurements when surface concentration was changed by compression (○) and by subsequent expansion (●).

surface pressures greater than about 5 dyn/cm diminished slowly with time, indicating that dissolution was occurring when the surface concentration was high. The rate of decay was roughly 0.1 dyn/cm per min at 10 dyn/cm and 0.5 dyn/cm per min at 18 dyn/cm. Because the rate of equilibration of the surface pressure after compression was more rapid at higher surface pressures than at lower, by performance of the experiments as rapidly as was consistent with equilibration it was possible to make measurements which were nearly reversible on the time scale of the experiments (cf. Figure 3). Still, because of the empirical shifts in concentrations, measurements for the diblock copolymers are less reliable quantitatively than those for the multiblock copolymers described below.

In Figure 3, findings for the PDMS-PS block copolymers of 0.71 and 0.76 fractional PS composition are compared with the behavior of PDMS homopolymer. Because the polymers were deposited over the space of 10 min, their concentrations have been scaled empirically to get agreement at low surface pressures with the findings for PDMS homopolymer. The plot is of surface pressure against surface concentration of PDMS, and surface pressures below 4 dyn/cm are not shown. Reversibility of the measurements is illustrated for copolymer 0.71. The strong effect of the dangling PS chains on the surface pressure is clearly noticeable on this linear plot. Where the surface pressure of PDMS homopolymer bends into a plateau, the surface pressure of the block copolymers continues to climb.

PDMS-P α MS Copolymers. Figure 4 plots logarithmic surface pressure against logarithmic surface concentration of PDMS. For these block copolymers with shorter dangling chains, the rate of spreading did not matter. For fractional P α MS compositions 0.14, 0.25, and 0.39 (not shown), surface pressures in the transition zone match those for PDMS homopolymers, but beyond the transition zone exceed them, just as for the PDMS-PS block co-

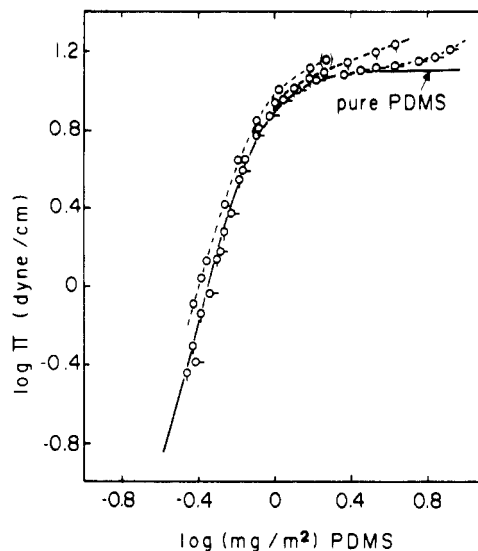


Figure 4. Surface pressure at 26 °C of tricresyl phosphate bearing PDMS homopolymer (solid line) and PDMS-P α MS multiblock copolymers, plotted logarithmically against surface concentration of PDMS. Points: ○, copolymer 0.14; □, copolymer 0.24; ○, copolymer 0.66.

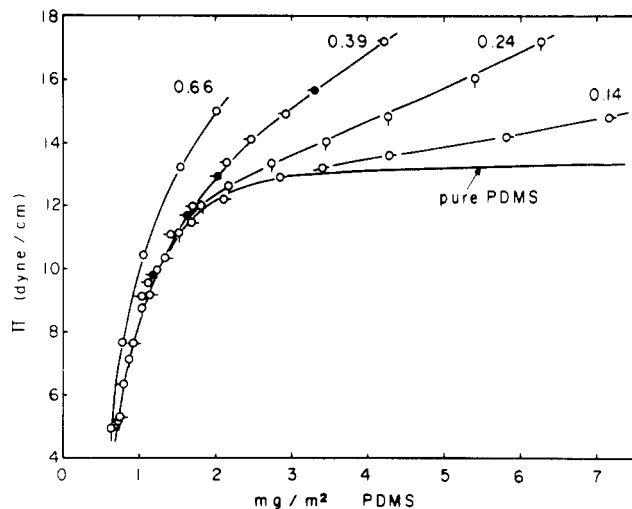


Figure 5. Surface pressure at 26 °C tricresyl phosphate bearing PDMS homopolymer (solid line) and PDMS-P α MS multiblock copolymers, plotted against surface concentration of PDMS. Fractional P α MS composition of copolymers is indicated in the figure. Reversibility of measurements for copolymer 0.39 is illustrated by comparison of measurements when surface concentration was changed by compression (-○) and by subsequent expansion (-●).

polymers. For copolymer 0.66, the surface pressure at all concentrations exceeds that attributable to the presence of PDMS blocks alone.

Figure 5 plots linear surface pressure against PDMS surface concentration for the entire family of PDMS-P α MS copolymers. Surface pressures below 4 dyn/cm are not shown. The curves fan out dramatically at high surface concentrations, to an extent that increases with increasing content of dangling chains. By doing experiments sufficiently rapidly at high surface pressures that the copolymers did not dissolve on the time scale of the experiments (typically 20 min), it was possible to make reversible measurements of surface pressure up to nearly 18 dyn/cm in regions where PDMS homopolymer of the same surface concentration was associated with a surface pressure of only 13 dyn/cm. Only for copolymer 0.66 were measurements not reversible, except at surface pressures below about 12 dyn/cm. Two measurements at higher surface

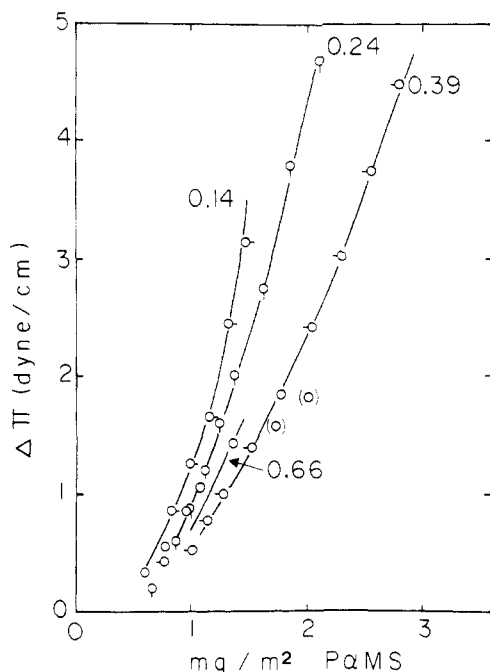


Figure 6. Supplementary surface pressure $\Delta\pi$ for PDMS- $P\alpha$ MS multiblock copolymers, plotted against surface concentration of $P\alpha$ MS, for copolymers of fractional $P\alpha$ MS composition as indicated. Points in brackets believed less reliable.

pressures are included for copolymer 0.66 to indicate the qualitative trend in the data. In Figure 5, reversibility is illustrated for copolymer 0.39, the copolymer which had the next-greatest tendency to dissolve at high surface pressures. The agreement between the open circles, indicating measurement during compression, and the filled circles, indicating measurement during subsequent expansion, is excellent.

Discussion

The supplemental surface pressure $\Delta\pi$ from dangling chains was calculated from the data in Figures 2-5, by subtracting at each PDMS surface concentration the surface pressure of PDMS homopolymer at the same surface concentration. For the multiblock copolymers, this difference is plotted in Figure 6 against the surface concentration of $P\alpha$ MS. The length of the dangling $P\alpha$ MS blocks is the same for all the polymers; it is the fractional $P\alpha$ MS composition that is varied. The curves for polymers of lower $P\alpha$ MS composition (i.e., higher PDMS composition) generally rise earlier and more steeply, probably reflecting interactions between the PDMS buoys and the dangling chains. However, these differences are small in view of the nearly fivefold difference in $P\alpha$ MS composition. For all the curves, the supplemental surface pressures rise faster than simply proportional to the $P\alpha$ MS surface concentration. They appear to extrapolate to $\Delta\pi = 0$ at about 0.5 mg/m^2 , suggesting that the character of the curves is different below this concentration. For the PDMS-PS diblock copolymers, the supplemental surface pressure varies with surface concentration in a similar fashion, as shown in Figure 7, and Figure 2 shows that here $\Delta\pi = 0$ within experimental uncertainty up to roughly 2 mg/m^2 dangling chains.

It is possible to gauge the concentrations of dangling chains in the surface layers. The onset of average overlap between chains should be roughly at the surface concentration $c^*_{2D} = M/N_A R_{G\parallel}^2$, where M is the polymer molecular weight per mole, N_A Avogadro's number, and $R_{G\parallel}$ the polymer radius of gyration parallel to the surface. The

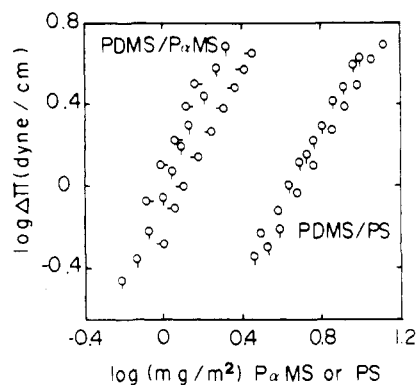


Figure 7. Supplementary surface pressure $\Delta\pi$ for PDMS- $P\alpha$ MS and PDMS-PS block copolymers, plotted logarithmically against surface concentration of $P\alpha$ MS and PS, respectively. Points: as in Figures 3 and 6.

value $R_{G\parallel}$ can be estimated as R_G (the radius of gyration in isotropic solution); and R_G can be roughly estimated as its value extrapolated to the block molecular weight according to known variations with molecular weight in toluene. For dangling PS chains with $M \approx 40,000$, one obtains²¹ $R_G \approx 65 \text{ \AA}$ and $c^*_{2D} \approx 0.5 \text{ mg/m}^2$. For dangling $P\alpha$ MS a similar calculation²² generates a similar estimate of c^*_{2D} , but this is probably quantitatively meaningless in view of the unknown average configuration of these short chains which are attached to the surface by both ends on the average. Despite the numerical uncertainties, it does appear that, for both families of block copolymers, the concentrations above which supplemental surface pressure was observed are reasonable ones for an effect attributed to osmotic interactions between overlapping dangling chains.

Logarithmic plots of supplemental surface pressure against surface concentration of dangling chains are shown in Figure 7. Curves through the points appear parallel within the rather large experimental uncertainty, although to avoid prejudicing the conclusions no curves have been drawn. For both families of copolymers, the findings are consistent with a power-law relation between $\Delta\pi$ and surface concentration, with power between 1.5 and 2, as predicted by eq 3. For the multiblock copolymers, the findings are shifted to lower concentrations, the lower the $P\alpha$ MS composition of the copolymer, indicating that the contributions of the dangling chains and of the PDMS monolayer are not strictly separable. However, for all the copolymers the character of curves through the points seems to be the same or nearly the same. The shifts are believed to reflect interpenetration of the dangling $P\alpha$ MS and of the collapsed PDMS monolayers, but no quantitative interpretation of the interaction is offered at this time. For the diblock copolymers, the onset of detectable supplemental surface pressure occurs at much higher surface concentrations of dangling chains. At the same surface concentration, $\Delta\pi$ from the PS dangling chains is about one-tenth that from the shorter $P\alpha$ MS dangling chains, consistent with eq 3 and the associated discussion.

It is puzzling that theoretical predictions based on a virial expansion for low volume fractions of polymer are consistent with the findings in Figure 7. The volume fractions of polymer in the surface layers were apparently rather high. For the PDMS-PS copolymers, arguments similar to those already made estimate the volume concentration to be $c^*_{3D} \approx 0.2 \text{ g/cm}^3$ at average overlap between chains. The polymers were then compressed a factor of 4 in surface concentration. One can speculate that competing influences on the free energy canceled one an-

other to some extent at high polymer volume fractions. Higher order terms in the virial expansion of eq 1, tending to be manifested in stronger dependence of surface pressure upon surface concentration, would have been offset if the dangling chains tended to escape the surface by dragging some portion of their PDMS buoys into the underlying liquid. Tendencies of the polymers to dissolve entirely at high surface pressures were in fact observed, as mentioned above. In future work it will be desirable to have more direct probes of surface structure than just the surface pressure.

Conclusions

The chief conclusion of this study is that osmotic interactions between polymer chains dangling into a liquid from an interface can contribute substantially to reducing the surface tension, as predicted by de Gennes,⁶ Alexander,⁷ and Cantor.⁸

Although the theoretical predictions are confirmed qualitatively, two features of the models⁶⁻⁸ in their present forms are found to be rather strong idealizations. First, the models assume that the adsorbing copolymer blocks are utterly insoluble in the underlying liquid, whereas experimentally the block copolymers showed marked tendencies to leave the liquid surfaces at high surface pressures. It is doubtful that a state of vanishing surface tension⁸ could be achieved experimentally in these systems. Second, the models assume that tendencies of dangling chains to stick to the surface or avoid it are negligible. In this study and in an earlier one,²³ some difficulty was encountered in finding an experimental system which avoided adsorption of the dangling chains. The compression experiments described above show that this was the case here; but in the system poly(ethylene oxide)-water, for example, the polymer forms a stable monolayer in spite of its solubility with water in all proportions.^{23,24} In the present system one expects some tendency of the dangling chains to avoid the surface, both the entropic reasons²⁵ and because the enthalpic interaction with the surface²⁶ may actually be repulsive. It appears that in future theoretical work, these idealizations should be relaxed.

Acknowledgment. This work was supported at the Collège de France by a grant from the Exxon Research and Engineering Co. to P.-G. de Gennes and by a C.N.R.S. A.T.P. "Surfaces" granted to C. Taupin. Its writing at the

University of Minnesota was supported by a grant from Medtronics to M. Tirrell. We are indebted to Professor J. V. Dawkins and to Dr. J. A. Semlyen for the generous gift of materials, and to Dr. R. Ober, Dr. C. Taupin, and Dr. R. Vilanove for discussions. S.G. is particularly grateful to Dr. C. Taupin for suggesting this study and welcoming him into her laboratory.

Registry No. Tricresyl phosphate, 1330-78-5.

References and Notes

- (1) M. J. Owen and T. C. Kendrick, *Macromolecules*, **3**, 458 (1970); A. G. Kanellopoulos and M. J. Owen, *J. Colloid Polym. Sci.*, **35**, 120 (1971).
- (2) J. Noolandi and K. M. Hong, *Macromolecules*, **15**, 482 (1982).
- (3) C. Price, *Pure Appl. Chem.*, **55**, 1563 (1983).
- (4) T. P. Lally and C. Price, *Polymer*, **15**, 325 (1974).
- (5) Z. Tuzar, P. Bahadur, and P. Kratochvil, *Makromol. Chem.*, **182**, 1751 (1981).
- (6) P.-G. de Gennes in "Solid State Physics", L. Liebert, Ed., Academic Press, New York, 1978, Suppl. 14; P.-G. de Gennes, public lectures, Collège de France, 1981-82.
- (7) S. Alexander, *J. Phys. (Paris)*, **38**, 983 (1977).
- (8) R. Cantor, *Macromolecules*, **14**, 1186 (1981).
- (9) L. Leibler, H. Orland, and J. Wheeler, *J. Chem. Phys.*, **79**, 3550 (1983).
- (10) N. L. Jarvis, *J. Colloid Interface Sci.*, **29**, 647 (1969).
- (11) S. Granick, *Macromolecules*, in press.
- (12) E. Riande, H. Markovitz, D. J. Plazek, and N. Raghupathi, *J. Polym. Sci., Part C*, **50**, 405 (1975).
- (13) J. V. Dawkins and G. Taylor, *Polymer*, **20**, 599 (1979).
- (14) P. Chaumont, G. Beinert, J. Herz, and P. Rempp, *Polymer*, **22**, 663 (1981).
- (15) W. D. Harkins and H. F. Jordan, *J. Am. Chem. Soc.*, **52**, 1751 (1930).
- (16) 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.
- (17) W. Fox, P. W. Taylor, and W. A. Zisman, *Ind. Eng. Chem.*, **59**, 1401 (1947).
- (18) M. K. Bennett and W. A. Zisman, *Macromolecules*, **4**, 47 (1971).
- (19) G. L. Gaines, Jr., "Insoluble Monolayers at Liquid-Gas Interfaces", Interscience, New York, 1966.
- (20) S. Granick, S. J. Clarson, T. R. Formoy, and J. A. Semlyen, *Polymer*, in press.
- (21) B. Appelt and G. Meyerhoff, *Macromolecules*, **13**, 657 (1980).
- (22) T. Kato, K. Miyaso, I. Noda, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 777 (1970); J. C. Selsler, *Macromolecules*, **14**, 346 (1981).
- (23) R. Ober and R. Vilanove, private communication.
- (24) R. L. Schuler and W. A. Zisman, *J. Phys. Chem.*, **74**, 1523 (1970).
- (25) J. H. Aubert and M. Tirrell, *J. Chem. Phys.*, **77**, 553 (1982).
- (26) A. J. Silberberg, *J. Chem. Phys.*, **48**, 2835 (1968).
- (27) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY, 1953.