Adsorbed Polymer Multilayers in a Bad Solvent

Introduction. Polymer adsorption is usually discussed in terms of the loop–train–tail conformation—each chain is attached to the surface at some site or sites.[1] This we will refer to as monolayer coverage. On the other hand, *multilayer* adsorption is ubiquitous. One encounters it every day; for example, in thick films of vapors adsorbed onto solids and of water adsorbed onto glassware.[2] The thickness of these films can be much larger than a molecular size.

Indeed, there are general thermodynamic arguments to expect, for any mixture in contact with a surface, that above the "wetting temperature" the surface can stabilize a microscopic phase that would still be unstable in the bulk. The physical reason is that an intervening multilayer region can lower the free energy of the interface between the adsorbed layer and the free solution.[3] These conclusions are inevitably based on various approximations and assumptions, however. In particular, no account is taken of a chain's internal structure. A chain becomes deformed when it is adsorbed, losing internal entropy. The natural question arises as to what relevance the general notion of the approach to wetting, while still in the one-phase region, may have for understanding adsorption of polymer chains.

Here we consider experimentally the conditions for multilayer adsorption of polymers. The results agree with general theories of wetting and imply that multilayers can persist up to temperatures considerably above the coexistence temperature (at least 10 °C). We also discuss tentatively the possibility that when the molecular weight of the polymer is sufficiently high, multilayer adsorption of chains may present interesting new varieties of behavior not encountered with small molecules.

Theory and Choice of Experimental Systems. A schematic diagram of the experiment is shown in Figure 1. We measured the surface excess (Γ, excess mass per area) as the temperature (T) was lowered in the direction of the coexistence temperature (T_{coex}), below which two macroscopic phases coexist. Only an adsorbed monolayer is expected far above T_{coex}. As T_{coex} is approached, the thickness of the adsorbed layer is expected to be less than macroscopic but thicker than a monolayer. Its composition will be approximately the same as that of the new polymer-rich phase, which appears at T_{coex}. In the experiments described below, the compositions of the polymer solutions studied (ϕ_1) were chosen to be below the critical composition (ϕ_c) so that the surface would be wetted by the phase of higher volume fraction (ϕ_2).[3]

For simple liquids the predictions are clear. If the attraction between adsorbate and the surface decays algebraically, then the forces are said to be long range and[3]

$$\Gamma \sim t^{1/\beta} \qquad (1)$$

Here t is the reduced temperature, $(T - T_{coex})/T_{coex}$. The most common example of this type of behavior is van der Waals attraction, with the exponent being the inverse power of the force. For instance, $\beta = 3$ for unretarded van der Waals attractive forces.

If the attraction decays exponentially, then the forces are said to be short range. A logarithmically divergent increase of surface excess is predicted:[3-5]

$$\Gamma \sim \ln \left[\Delta\mu/kT\right] \qquad (2)$$
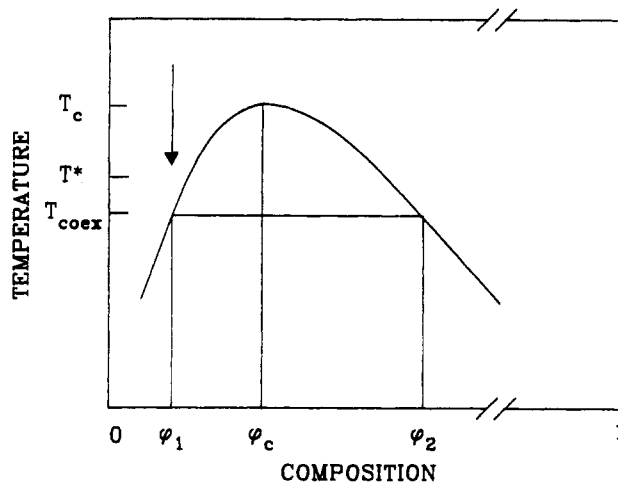
$$\Gamma \sim \ln t \qquad (3)$$

Figure 1. Schematic diagram of the phase diagram of the polymer solutions. The surface excess, Γ, was measured as the temperature, T, was lowered toward the coexistence temperature, T_{coex}, below which two phases coexist. In order to achieve the condition that the surface was wetted by the phase of higher volume fraction, the volume fraction of the polymer solution was chosen to be below the critical point.

Here the incremental chemical potential, $\Delta\mu$, is the chemical potential difference from that at the coexistence temperature, and k is the Boltzmann constant. We are using T_{coex} as a synonym for the temperature at which the binodal curve is crossed.

However, the wetting phenomena associated with high molecular weight polymers can be anticipated to be more complex because polymer chains are subject to both intermolecular and intramolecular "condensation" in dilute solution at temperatures below the Θ temperature. There is expected to be a critical temperature defining the incipient intramolecular condensation ("collapse"). We are indebted to Dr. J. Douglas for calling our attention to this complication.

The coil–globule transition of dilute polymer chains (so-called "polymer collapse") has seen considerable study over the years, and the point of polymer collapse has been analyzed in various formulations.[6] One way to formulate the problem is to consider the Fixman dimensionless excluded-volume interaction z_2[7-9]

$$z_2 = kM^{1/2}|T - T_\Theta|/T \qquad (4)$$

Here k is a constant related to monomer dimensions and T_Θ is the bulk Θ temperature. For polystyrene in cyclohexane, the result is a predicted instability when $z_2 > \approx 20$–30.[7,8]

This limit of the stability of chain dimensions is consistent with careful experiments.[10] For $z_2 > 20$–30, rather inconsistent degrees of chain contraction have been reported; the experimental results seem to depend to an extreme degree on experimental conditions.[6] These variable results have been variously associated with long-lived metastable states[10] or perhaps a true bifurcation of equilibrium states.[7,8] Regardless of the final explanation, the onset of instability appears to be well described by the above limit of z_2. We used this limit as a phenomenological guide to the conditions under which to expect rapid equilibration of chain dimensions.

With these considerations in mind, two polymer samples were selected for investigation. The molecular weight of the first sample (polymer A) was sufficiently low that the issue of polymer collapse was avoided at all temperatures. Experiments were also performed by using a fraction of

Table I
Characterization of the Polystyrene Standards

code	$M_w{}^b$	$M_w/M_n{}^b$	$R_G,{}^c$ Å	$\phi_1{}^d$	$T_{cloud},$ °C	$T^*,$ °C
A	43 900^e	1.01	59	6.41×10^{-3}	8.1	8.1
B	355 000^e	1.02	167	4.32×10^{-4}	19.1	21.2

^{a} M_w is the weight-average molecular weight. M_w/M_n is the ratio of M_w to the number-average molecular weight. R_G is the unperturbed radius of gyration in bulk solution. ϕ_1 is the volume fraction of polymer in the solution. T_{cloud} is the cloud point measured for the bulk solution. T^* is the temperature at which measurements of surface excess became unstable. ^{b} Manufacturer's data. ^{c} Calculated from ref 14. ^{d} Calculated at 25 °C. ^{e} Protio polystyrene, obtained from Toyo Soda.

higher molecular weight (polymer B), in which case z_2 exceeded the range 20–30 while still in the one-phase region. Characteristics of the polystyrenes studied (obtained from Toyo Soda) are given in Table I.

Experimental Section. The experimental setup,[11] surface preparation,[12] and calibrations to distinguish between adsorbed polymer and polymer in solution[12,13] were the same as those previously described for other experiments measuring adsorption–desorption kinetics[11,12] and enthalpic effects in polymer adsorption.[13]

The surface excess of polystyrene, adsorbed to oxidized silicon from cyclohexane, was monitored in situ by using Fourier transform infrared spectroscopy (FTIR) in the mode of attenuated total reflection (ATR). Cyclohexane (Baker) was freshly distilled and dried with molecular sieves. The volume fraction of polymer was calculated by weight, assuming a partial specific volume of 0.9293 cm^3 g^{-1} at 25 °C.[14] The cloud points of the polymer solutions, T_{cloud}, were measured visually. We expect that $T_{cloud} = T_{coex}$ within the experimental uncertainty of temperature measurement and control (± 0.1 °C).

The polymer solutions were introduced into the sample cell at the highest experimental temperatures. The temperature was lowered step by step, pausing for 2–5 h at each temperature to wait for equilibration. One could imagine that the growth of surface excess that we report below stemmed from fractionation of the longer chains to the surface. Control experiments, in which the solution was replaced by fresh solution while an experiment was in progress, ruled out this possibility because no marked increase in adsorption was noted.

Control experiments confirmed reversibility when the temperature was first lowered and then increased.

Polymer A. The findings obtained by using polymer A (low molecular weight) are discussed. The volume fraction was $\phi_1 = 6.41 \times 10^{-3}$, selected so that T_{cloud} would fall at a convenient temperature. Equilibration was rapid (<30 min) at every temperature down to the cloud point, T_{cloud}. At $T < T_{cloud}$, adsorption measurements did not equilibrate on the experimental time scale, presumably owing to sedimentation of the denser phase away from the ATR crystal toward the bottom of the sample cell.

The surface excess as a function of temperature is plotted in Figure 2. The surface excess rose monotonically with decreasing temperature. It more than doubled over a range of 10 °C, still within the single-phase region. A qualitative test of whether this surface excess represented monolayer or multilayer coverage was to flow the polymer solution past the surface. Substantial desorption resulted at the lower temperatures. This indicated that multilayers were attached to the surface only loosely.

The central result of this paper is that these data are well described by eq 3. This may be seen in Figure 3, where Γ is plotted as a function of $\ln[(T - T_{cloud}/T_{cloud})]$.
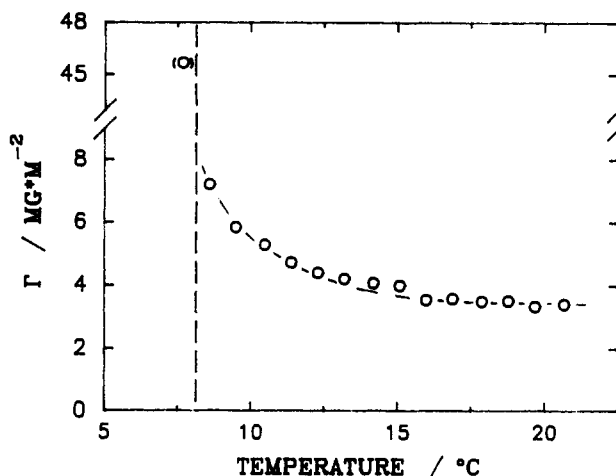

Figure 2. Surface excess of polymer A ($M_w = 43\,900$) plotted versus temperature. The open circle in parentheses indicates an unstable measurement (as defined in the text). Vertical dashed line shows the cloud-point temperature of the bulk solution.
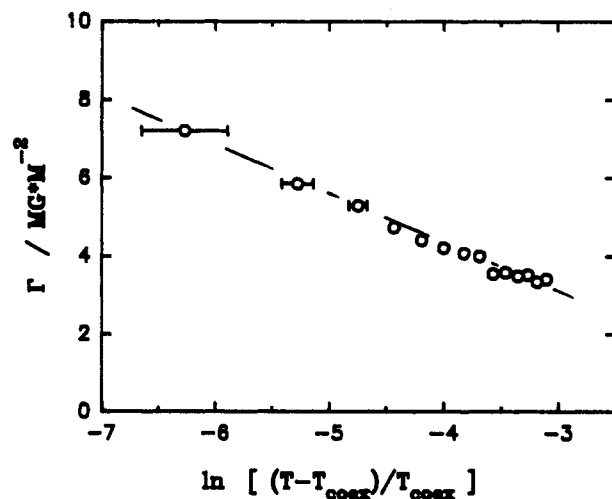

Figure 3. Surface excess of polymer A plotted against the logarithmic reduced temperature, $(T - T_{coex})/T_{coex}$.

The data do not fit eq 1 or other power law behavior. To conclude that multilayer buildup in a complex polymer system obeys orthodox behavior for short-range forces is interesting and gratifying, though it raises the question of the correct molecular interpretation of this force. The prefactor of the logarithmic divergence, 3.2 mg m^{-2} per logarithmic decade, is also of interest; see the discussion of eq 6. A study of how the prefactor varies with solution composition is in progress.

Let us estimate the area-averaged layer thickness. Over the range of temperature shown in Figure 2, the additional adsorption measured was approximately 4 mg m^{-2}. Let Γ' be this number, the largest measured surface excess owing to multilayers. Then

$$L = \Gamma'/\rho_2 \tag{5}$$

One knows, from previous measurements of the coexistence curve of polystyrene solution of similar molecular weight in cyclohexane, that the density of the polymer-rich phase is $\rho_2 \approx 0.4$ g cm^{-3} at this overall solution composition.[15] If $\Gamma' = 4$ mg m^{-2}, then $L \approx 100$ Å, which is already less than the radius of gyration (see Table I). At a higher temperature, where Γ' is less, perhaps only 0.4 mg m^{-2}, then $L \approx$ 10 Å, which is scarcely more than a segmental thickness! Taken literally, this would imply extreme deformation of the chains adsorbed within the multilayer, which does not seem reasonable on physical grounds. A possibility is that
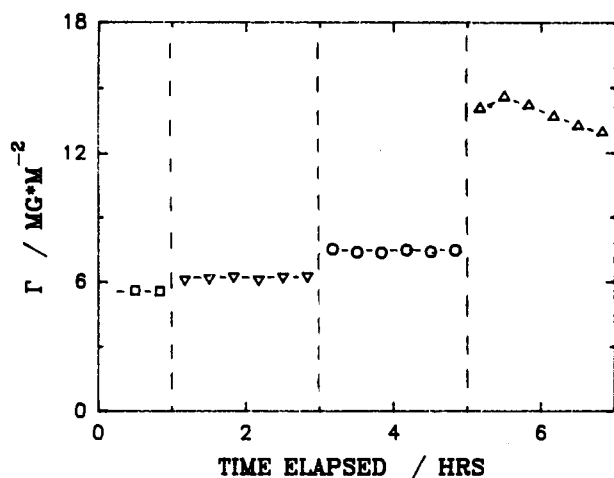
Figure 4. Surface excess of polymer B plotted against time elapsed. The origin of the abscissa is 25 h into an experiment. The temperature was changed incrementally: (□) 22.5 °C, (▽) 22.0 °C, (○) 21.5 °C, (△) 21.1 °C.

this is a case of *partial* wetting rather than complete wetting, i.e., that the multilayer zone is comprised of microscopic droplets rather than a homogeneous film.

Growth of L (adsorbed layer thickness) with t (reduced temperature) should be proportional to the correlation length of short-range interactions,[16,17] ξ:

$$L \sim \xi \ln t \tag{6}$$

The L estimated in the previous paragraph then gives $\xi \approx 25$ Å—on the order of R_G (cf. Table I). A study of changes in this behavior with solution composition is in progress.

It is interesting to conclude that, over the temperatures investigated, there was no obvious threshold temperature above which multilayer adsorption did not contribute at some level to the surface excess. It is worth noting that similar findings have been seen in other systems. Equation 3 has described adsorption from binary mixtures of cyclohexane and aniline;[18] surface melting of very thin films of Ne on graphite,[19] of O_2 on graphite,[20] and of methane on MgO;[21] and molecular dynamics simulations of small particles near a wall.[16] This was not necessarily expected since the original derivations of eq 2 assumed the multilayer's interfacial tension to be that of a bulk phase of composition ϕ_2.[4,5]

As noted in the Experimental Section, control experiments confirmed reversibility when the temperature was first lowered and then increased.

Polymer B. We turn now to experiments using a sample of much larger molecular weight, polymer B. Again the volume fraction, $\phi_1 = 4.32 \times 10^{-4}$, was selected so that T_{cloud} would fall at a convenient temperature. The results agree with those for polymer A in some respects while differing in others. Figure 4, in which Γ is plotted against time elapsed after 25 into an experiment, illustrates the difficulty encountered in reaching equilibration. Equilibration, although rapid at temperatures 21.5 °C and below, was not obtained on the experimental time scale at $T \leq$ 21.1 °C. The corresponding reduced expansion parameter was $z_2 \geq 27$, just in the range for polymer collapse anticipated by the discussion of eq 4. It is true that long equilibration times of the surface excess can arise from slow diffusion in solution. However, this should not explain the present findings since the equilibration of surface excess was rapid for polymer A.

A plot of the surface excess as a function of temperature for polymer B is shown in Figure 5. Unstable measurements such as those shown in Figure 4 are bracketed. As
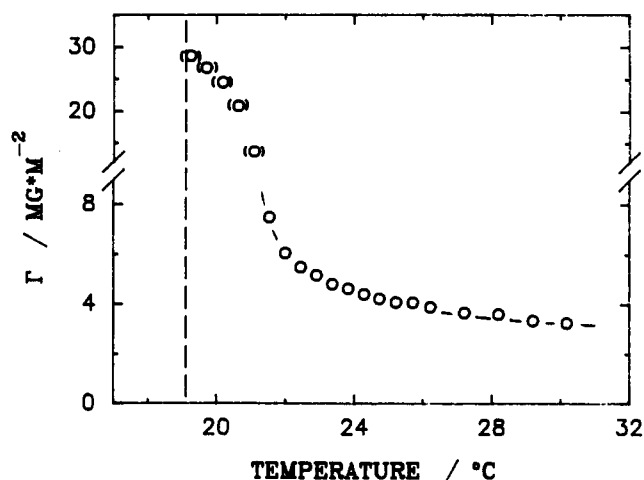

Figure 5. Surface excess of polymer B ($M_w = 355\,000$) plotted against the temperature. Open circles in parentheses indicate unstable measurements (as defined in the text). The vertical dashed line shows the cloud-point temperature of the bulk solution.
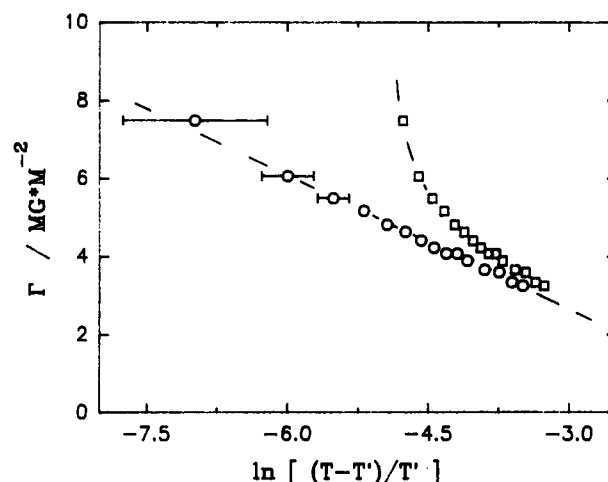

Figure 6. Surface excess of polymer B plotted against the logarithmic reduced temperature in two different ways: (□) T' = T_{cloud}, (○) T' = 21.2 °C = T^*.

seen before with polymer A, the surface excess rose monotonically with decreasing temperature, more than doubling over the range of temperatures investigated. The layer was again fragile in the sense that it was swept away by flow of the surrounding solution past it.

Again, as with polymer A, the data do not obey a power law (eq 1). Figure 6 shows that $\Gamma \sim \ln [(T - T_{coex})/T_{coex}]$ is not obeyed either. In these comparisons, of course only the instances of equilibrated surface excess are analyzed.

A provocative observation is that the data *do* fit the relation $\Gamma \sim \ln [(T - T^*)/T^*]$; here T^* is the temperature below which unstable measurements were obtained. Note that T^* (21.2 °C) is less that the critical temperature, T_c (cf. Figure 1), which may be readily estimated[22] to be 26.6 °C.

There are two avenues of possible explanation. One is that T^* reflects instabilities in bulk solution, as discussed above. On the other hand, it may be that T^* is actually a surface transition temperature. The physical origin of a surface thermodynamics different from that in the bulk is that the chemical potential at a surface depends not only on the temperature and pressure but also on the strength of the surface–adsorbate interaction.[3] Surface wetting transitions have been considered as theoretical possibilities[4,23,24] but have not, to our knowledge, been observed, at any rate in a polymer system.

These alternatives as to the microscopic origin of $T^* > T_{coex}$—internal condensation of coils into globules or a surface adsorption transition—may be distinguished by experiments (in progress), in which multilayer adsorption is measured as the strength of the surface–polymer atttraction is varied. If T^* reflects the former possibility, then multilayer adsorption should be little affected.

One notices in Figure 6 that the slope of Γ versus log $(T - T^*)$ actually coincides with that obtained for Γ versus log $(T - T_{coex})$ for polymer A (see Figure 3). This intriguing observation suggests that the correlation length of the short-range interactions may be the same or similar in the two systems, but no detailed discussion is offered at present.

What of possible artifacts? The possibility should be considered that these observations reflect residual polydispersity in the polymer, perhaps fractionation of a high molecular weight tail of the distribution onto the surface. However, a coexistence curve is well-defined even for polymer samples that are far more polydisperse.[25] Changing the polymer solution to a fresh sample would be expected to result in additional adsorption if adsorption resulted from fractionation, yet, as noted above, control experiments failed to detect this. Finally, the generality of the effect was verified by using a second sharp fraction of high molecular weight (deuterated polystyrene purchased from Polymer Laboratories, $M_w = 550\,000$, $M_w/M_n = 1.05$). For these reasons, we consider it unlikely that fractionation to the surface explains these observations.

Discussion and Conclusions. Although this is, to the best of our knowledge, the first experimental demonstration of adsorbed polymer multilayers, it should be noted that their incidence was anticipated nearly 20 years ago by calculations of Silberberg.[26] Numerical calculations of van der Schee, using the Scheutjens–Fleer theory, also suggested the logarithmic divergence of Γ,[27] though its fundamental origin was not recognized. On the experimental side, Findenegg[28] made an early ellipsometric study of the wetting of polystyrene–cyclohexane solutions at the vapor interface. The possibility of multilayers was considered by Terashima.[38] A study of Kawaguchi and Takahashi[29] found enhanced adsorption of polystyrene from cyclohexane onto a chrome plate even at temperatures above T_θ; in hindsight this may be due in part to multilayers as well as to the proposed changes in solvent quality. Similar changes of adsorption with temperature, at $T < T_\theta$, are apparent when one looks back at experiments that employed the surface forces technique at variable temperatures near T_θ;[30,31] it is interesting to conclude that those experiments may have involved polymer multilayers rather than monolayers as was assumed. For poly(dimethylsiloxane)–bromocyclohexane solutions at the air-solution interface below the θ temperature, X-ray reflectivity experiments of Barton are presently seeking to probe the segment density profile.[32]

The conclusion of multilayer adsorption was also drawn from the enhanced (but still microscopic) adsorption observed as nonsolvent was added to polystyrene solutions.[33]

Multilayers are also expected to form in an analogous situation, the surface segregation of polymer blends.[34-37]

In conclusion, the pronounced increase of surface excess near T_{coex} reported here for two polystyrene samples is strong, although indirect, evidence of the buildup of multilayers. Measurements using a sample of low molecular weight agree strictly with the general thermodynamic expectation for any liquid mixture whose adsorption is dominated by short-range forces. Measurements using a sample of higher molecular weight also support the buildup of multilayers but in addition suggest the occurrence of a multilayer transition temperature, T^*, higher than T_{coex} in the bulk solution.

References and Notes

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