Surface Concentration of a Styrene–Dimethylsiloxane Block Copolymer in Mixtures with Polystyrene

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ABSTRACT: A carefully fractionated block copolymer of composition styrene$_{75}$–dimethylsiloxane$_{77}$ was added in low concentrations (0.05–5 wt %) to polystyrene, $M = 9290$. The time-dependent surface tensions of these blends were measured at temperatures of 160–200° using the pendent-drop method. The surface tensions of toluene solutions of the copolymer only, at room temperature, were also determined. At the lower concentrations and temperatures, the initial time evolution of the polymer blend surface tensions appears to be governed by diffusion, and it is possible to estimate a diffusion constant for the copolymer in polystyrene from the data. After the initial, apparently diffusion-limited stage, the surface tension continues to decrease slowly over periods of several hours, finally approaching the surface tension of pure polydimethylsiloxane, at least for copolymer concentrations of greater than 0.2%. We have found the pendent-drop method to be of limited use for estimating equilibrium surface tensions in these systems because of the occurrence of drop detachment.

It has long been recognized that surface properties of solid polymers may be modified by incorporation of additives which migrate to the polymer surface during processing. Long-chain amides incorporated in polyethylene[2] or vinylidene chloride–acrylonitrile copolymer[3] concentrate at the surface, providing effective lubrication of films of these materials. Similarly, certain fluorinated compounds reduce both wettability[4] and friction[5] when they are incorporated in various polymers. Zisman and his coworkers were the first to suggest that silicone compounds might exhibit surface activity in organic polymers.[4,5] Recently, LeGrand and Gaines[6] and, independently, Owen and Kendrick[7] have shown that dimethylsiloxane–organic block copolymers do concentrate at the surface when they are added, in low concentrations, during fabrication of solid organic homopolymers. These block copolymers appear to be particularly suitable additives for practical application because they are effective at very low levels, resist removal from the surface by rinsing, and can be synthesized in a wide range of molecular geometries.

Two phenomena which may be expected to be of major importance in such applications are the extent of surface concentration (at equilibrium) and the rate at which it develops. Both will certainly depend on the composition and structure of the block copolymer. In the present study we have examined the time dependence of surface tension lowering in a polystyrene melt to which have been added small concentrations of a well-characterized styrene–dimethylsiloxane block copolymer.

Experimental Section

Materials. The styrene–dimethylsiloxane block copolymer was synthesized by the anionic polymerization of styrene with n-butyllithium as initiator, followed by addition of hexamethylcyclotrisiloxane, and terminated with acetic acid. To block the terminal hydroxyl group and avoid any further condensation during subsequent handling, the preparation was end-capped with bistrimethylsilylacetamide (2 hr reflux in benzene with a 15-fold excess). This procedure eliminated the band in the ir spectrum at 3680 cm^{-1}. The sample was then divided into seven fractions by foaming as an 0.5% solution in toluene.[8] Analysis of these fractions indicated that in the original preparation the polystyrene block was of quite uniform size while the polydimethylsiloxane blocks ranged in degree of polymerization from about 40 to 80. A middle fraction, consisting of about 20% of the original material, was used in the present experiments. It was characterized by osmotic molecular weight determination (benzene 35°) and elemental analysis for Si; these measurements indicated $M_n = 13{,}500$, with the average DP of the styrene and siloxane blocks being 75 and 77, respectively (42.3 wt % dimethylsiloxane).

Polystyrene, $M_n = 9290$, was from the same lot used in our previous study.[9] Benzene and toluene of reagent grade were purified by percolation through alumina–silica gel columns before use.

Methods. Surface tension of dilute toluene solutions of the copolymer were measured by the ring method. No time-dependent effects were noted. Surface tensions of the polymer melts were determined by the pendent-drop method as previously described.[9] Homopolymer–copolymer blends were prepared by freeze-drying benzene solutions of appropriate composition. The density of the block copolymer was measured dilatometrically; in the range $t = 140$–$200°$, the specific volume was given by

$$V = 0.9628 + (7.44 \times 10^{-4}t)$$

The densities of the blends were calculated on the basis of their compositions from these data and the previously determined densities of the styrene homopolymer.

Results

Surface Tension of Copolymer Solutions in Toluene. Figure 1 shows the measured surface tensions of solutions of the styrene–siloxane block copolymer in toluene. Also shown is the curve which is calculated for solutions of a monodisperse polydimethylsiloxane of $M = 5710$ using lattice theory.[10] (We have previously found this theory to be in good agreement with experiment for polydimethylsiloxane solutions when allowance is made for molecular weight distribution.[10,11]) At concentrations below about 5 vol % dimethylsiloxane, the surface tensions of the block copolymer solutions appear to be nearly the same as those calculated for the siloxane block alone. At higher concentrations, the block copolymer produces greater surface tension lowering

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TABLE I

MINIMUM OBSERVED SURFACE TENSIONS (DYN/CM) FOR POLYSTYRENE + STYRENE–DIMETHYLSILOXANE COPOLYMER BLENDS[a]

Temp, °C	Homopolymers		Copolymer concentration, wt %			
	PS[b]	PDMS[c]	0.05	0.1	0.2	5.0
166	29.9	12.8		17.3 (450)		13.8 (220)
171	29.5	12.6	18.1 (180)			
185	28.7	11.9	16.2 (130)	14.1 (240)	12.9 (175–240)	12.6 (60–100)
200	27.7	11.2	14.7 (240)	13.9 (150)	13.5 (90)	11.9 (75–105)

[a] Numbers in parentheses indicate age of drop, in minutes, for the observed value. [b] See ref 9. [c] R.-J. Roe, *J. Phys. Chem.*, **72,** 2013 (1968).

than would the homopolymer at the same siloxane concentration. This may reflect the progressively worse solvent environment for the silicone as the amount of polystyrene increases in the copolymer solutions. In this regard, it is interesting to note that these deviations become appreciable near the concentration where phase separation is first observed in a mixed solution of styrene and siloxane homopolymers, indicated by the arrow in the figure.

Attempts to Estimate Equilibrium Surface Tension in Polymer Melts. The pure copolymer, even at temperatures above 250°, did not form a clear fluid melt. A visible turbidity was present, and even though the material flowed readily from the syringe, we were not able to obtain "normal" drop shapes. Elliptical or blunted pendent drops were formed, and allowing them to hang on the syringe tip for periods of up to 3 hr (at 225°) did not eliminate the initial deformed drop shape. We conclude that these melts are viscoelastic, presumably because of the well-known domain formation in block copolymers of incompatible segmers. No estimate of the surface tension of the pure copolymer is available, therefore.

No such difficulties were encountered with the mixtures of the copolymer with polystyrene (up to 5 wt % copolymer). The melts were optically clear or only slightly hazy, and hydrodynamic equilibrium (as judged from consistency of $1/H$ values) was achieved within a few minutes of drop formation. The approach to surface tension equilibrium, however, was very slow, especially for the lower concentrations and temperatures. The tendency for the pendent drops to fall from the syringe tip as the surface tension decreased proved to be a severe limitation on this method. In a few cases with the highest concentrations and temperatures, surface tension values appeared to reach a constant value (±0.2 dyn/cm) after an hour or so, but in some experiments the surface tension was still decreasing at the time when the drop detached or became unmeasurable (usually 2–4 hr; 7.5 hr in one run). It seems likely that the measurement of equilibrium surface tensions in systems of the sort we have studied could be accomplished better by such techniques as the Wilhelmy method described by Dettre and Johnson[12] or the sessile bubble method.[13]

In Table I the lowest surface tensions which we observed, together with the ages of the drops, are recorded. Also listed are equilibrium surface tension values at the corresponding temperatures for the anionic polystyrene of molecular weight 9290 and a high molecular weight polydimethylsiloxane. The results for 5% copolymer and 0.2% copolymer at 185° may represent equilibrium values. In each of these cases the observed values remained practically constant for a substantial time before the final measurement. They are all within 1 dyn/cm of the surface tension of pure polydimethylsiloxane and about 16 dyn/cm below the surface tension of polystyrene.

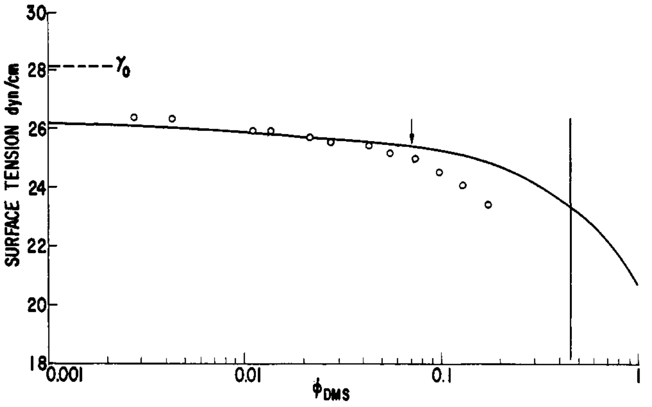

Figure 1. Surface tension of toluene solutions of block poly(styrene$_{75}$-*co*-dimethylsiloxane$_{77}$), at 24°, *vs.* volume fraction of siloxane in solution, on a log scale. Circles are experimental points. Curve represents values calculated for toluene solutions of dimethylsiloxane homopolymer of DP 77, using lattice theory (β = 43.5 × 10^{-16} erg/molecule).[10] Vertical bar corresponds to composition of the pure copolymer. Arrow denotes the point where phase separation is observed in a mixed toluene solution containing approximately equal amounts of styrene and siloxane homopolymers of molecular weight ~5000. γ_0 is the surface tension of toluene.

These values are in marked contrast to those obtained for solutions of the copolymer in the small-molecule solvent at room temperature. As indicated in Figure 1, toluene solutions in the concentration range 0.05–5% have surface tensions of 26.9–25.7 dyn/cm, compared with the pure solvent value of 28.1 dyn/cm and the surface tension of high molecular weight polydimethylsiloxane of 20.7 dyn/cm at 24°. This difference most probably reflects further the poor solvent environment for the silicone afforded by the polystyrene.

Rate of Surface Tension Lowering. Photographs of drop profiles were made at intervals of 2–3 min after drop formation to periods up to several hours. As already noted, hydrodynamic equilibrium generally appeared to be attained within a few minutes (all drop photographs for which $1/H$ values were not consistent within 0.5% were discarded). In all runs, the surface tension decreased monotonically with time.

A difficulty in the analysis of the data arises from the uncertainty in the time to be assigned to the initial formation of the surface. The manipulations required to form a drop of the proper size in our apparatus required approximately 1 min. In some runs the flow properties of the polymer melts were

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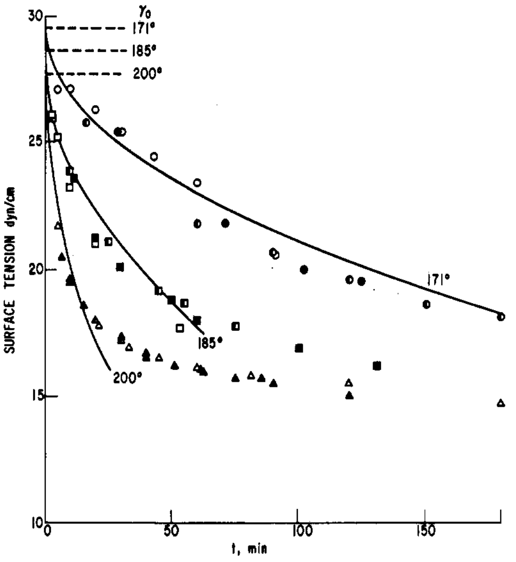

Figure 2. Surface tension as a function of time for blend of polystyrene + 0.05 wt % poly(styrene$_{75}$-*co*-dimethylsiloxane$_{77}$). Experimental points: ○, 171°; □, 185°; △, 200°; shading indicates different runs. Curves are calculated for diffusion-controlled adsorption; see text. γ_0 is the surface tension of pure polystyrene, $M = 9290$, at the indicated temperature.

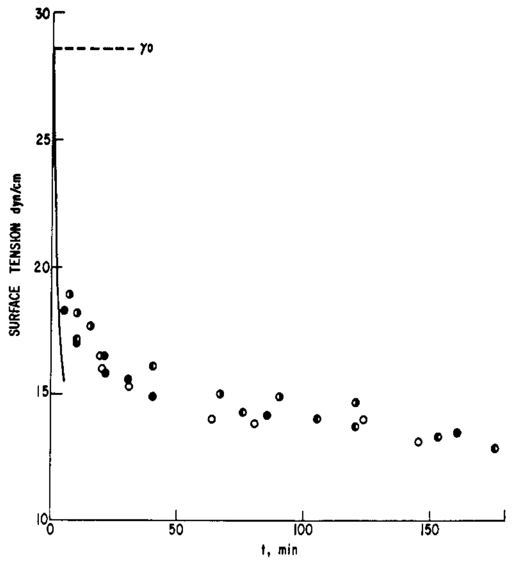

Figure 4. Surface tension for blend of polystyrene + 0.2 wt % poly(styrene$_{75}$-*co*-dimethylsiloxane$_{77}$) at 185°. Shading of points indicates different runs. Curve is calculated for diffusion-controlled adsorption; see text. γ_0 is the surface tension of pure polystyrene, $M = 9290$, at 185°.

such that it was found necessary to form a drop and then partly retract it into the syringe to prevent early detachment. In these cases periods of up to 3 min were actually occupied in forming the drop; during this time the surface was both expanded and contracted. For analysis we have taken the age of the surface as the time from the initiation of drop formation. Clearly this is a maximum age, in every case slightly larger than the "true" age, and for the data at short times must be considerably in error.

The initial rate of surface tension lowering was found to increase markedly as either copolymer concentration or temperature was increased. With 5% copolymer at all temperatures, the earliest measurements (drop ages of 3–8 min) all indicated surface pressures, *i.e.*, surface tension lowerings, of 13–15 dyn/cm, with the subsequent decrease (of 1–3 dyn/cm) continuing over several hours.

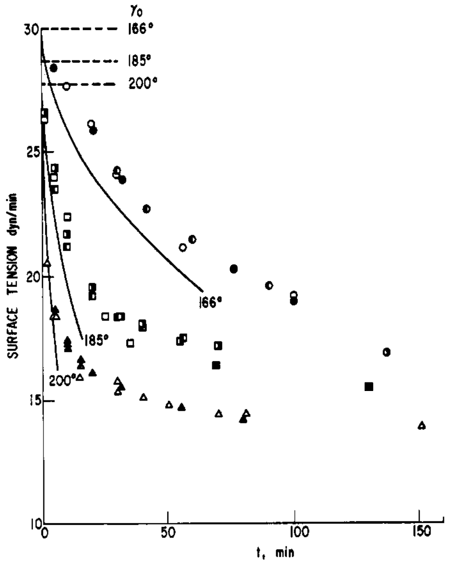

Figure 3. Surface tension for blend of polystyrene + 0.1 wt % poly(styrene$_{75}$-*co*-dimethylsiloxane$_{77}$). Experimental points: ○, 166°; □, 185°; △, 200°; shading indicates different runs. Curves are calculated for diffusion-controlled adsorption; see text. γ_0 is the surface tension of pure polystyrene, $M = 9290$, at the indicated temperature.

For the lowest copolymer concentrations and lower temperatures, however, the decrease was more gradual over the entire period of the experiment. Figures 2–4 show the results over a period of three hours for the lower concentrations. (Measurements were also performed with 0.2% copolymer at 200°; the values obtained ranged from 20.2 dyn/cm at 5 min to 13.1 dyn/cm at 180 min, but they were erratic. Discrepancies between different runs at the same elapsed times were as much as 4 dyn/cm, and these results are not presented here.)

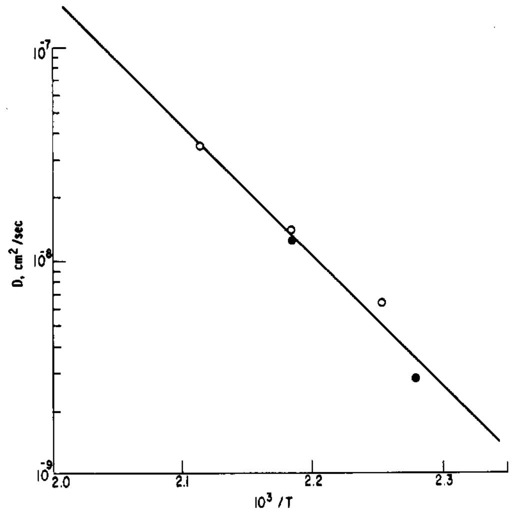

Figure 5. Arrhenius plot of diffusion constants, as estimated from equation 3, for poly(styrene$_{75}$-*co*-dimethylsiloxane$_{77}$) in polystyrene. Copolymer concentration (○) 0.05%, (●) 0.1%.

Discussion

The Nature of the Surface Layer at Equilibrium. Our inability to establish unambiguous values of equilibrium surface tension limits interpretation. However, the minimum observed values (Table I) strongly suggest that at concentrations of greater than 0.2% of the copolymer in polystyrene (and hence, by implication, for the neat copolymer as well) the surface tension is near that of polydimethylsiloxane. Other studies have shown that propylene oxide–ethylene oxide[14] and dimethylsiloxane–polyether[15] block copolymers have surface tensions equal to that of the corresponding homopolymer of lower surface tension, as long as the block of that species is sufficiently long. These results also suggest that our copolymer, with 77 dimethylsiloxane units, might be expected to have the surface tension of a pure siloxane.

Solutions of more than a fraction of 1% of dimethylsiloxane–polyether copolymers in water and polyglycol also exhibit the surface tension of pure polydimethylsiloxane when the degree of polymerization of the siloxane block is greater than about 35.[15–17] Similarly, Owen and Kendrick[7] found that the addition of 1% styrene–dimethylsiloxane block polymers with siloxane DP of 77 or 96 to polystyrene produced critical surface tensions for wetting equivalent to that of homopolydimethylsiloxane. On the other hand, the surface tensions of solutions of these materials in styrene monomer or benzene were not lower than 23.5 dyn/cm at room temperature—2–3 dyn/cm greater than that of the neat silicone. They concluded that insolubility of the siloxane block in the solvent used was required to achieve the homopolymer surface tension. The same conclusion may be reached from our observation of the difference of behavior of the block copolymer in toluene and polystyrene; in this case, of course, incompatibility or insolubility in the polymeric solvent reflects the usual immiscibility of two polymers arising from the low entropy of mixing.[18]

These results suggest that in those cases where the low surface tension block is sufficiently long and insoluble in the solvent (for whatever reason), the surface layer at equilibrium is essentially composed of that species, with nearly complete exclusion of both solvent molecules and segments of the other block. This may represent the surface analog of domain formation in the bulk block copolymer. We do not know whether in the mixed systems we have studied such domains are present in the bulk.

It has been suggested[17] that the surface-active properties of block copolymers may best be compared with those of conventional surfactants. Domains in bulk bear certain resemblances to micelles in small-molecule surfactant solutions. However, the formation of a surface layer from which solvent is excluded and whose tension approximates that of a single component of the system is clearly different from the behavior of surfactant solutions above (but near) the cmc. Thus, while there are similarities, it is not yet clear how far the analogy should be carried. It may be that the liquid-crystalline phases in amphiphile–water systems at high solids content will provide useful comparisons.

Rate Processes. The kinetics of adsorption at the surface of a solution has been the subject of much study. In any particular system, several factors in principle may govern the rate process.[19] It is clear, however, that adsorption cannot occur until a sufficient number of surface-active molecules have arrived at the interface and, hence, that under some conditions bulk diffusion may be expected to control the rate. A detailed analysis of diffusion-controlled adsorption kinetics was provided by Ward and Tordai;[20] their general equations have been applied and modified by many subsequent workers. As they pointed out, if the surface is initially very sparsely populated with adsorbable molecules, the early stage of the adsorption process may be described by the equation, originally given by Langmuir and Schaefer[21]

$$M = 2c_0(Dt/\pi)^{1/2} \tag{1}$$

where M is the surface concentration at time t, c_0 is the constant bulk concentration, and D is the diffusion constant.

If M, the surface concentration, is taken as equal to the surface excess $\Gamma_2^{(1)}$ and the bulk concentration remains constant, eq 1 can be combined with the approximate form of the Gibbs adsorption equation

$$\Gamma_2^{(1)} = -(1/RT)(\partial\gamma/\partial \ln c) \tag{2}$$

to yield

$$\Pi = 2RTc_0(Dt/\pi)^{1/2} \tag{3}$$

where Π, the surface pressure, is the difference between the initial (clean surface) tension and the surface tension, γ, at time t.

Despite the simplicity of eq 3 and its resemblance to eq 1, it is important to recognize the assumptions implicit in it. The derivation of eq 1 requires that Fickian diffusion with a concentration-independent D govern adsorption and that every molecule arriving at the surface adsorb instantly—*i.e.*, there is neither a significant energy barrier to adsorption itself nor enough adsorbed material in the surface to produce a sensible back-diffusion into the bulk. In addition, utilization of the approximate Gibbs equation implies that the activity coefficient of the diffusing solute is unity. Equating M to $\Gamma_2^{(1)}$ requires both instantaneous local equilibrium at the surface and restricts the bulk concentration to values negligible compared to M. It is clear, therefore, that (3) can only be expected to apply for very low values of c_0.

Where eq 3 applies, however, it is to be expected that the surface pressure will be proportional to $t^{1/2}$ and the slope of the Π–$t^{1/2}$ plot at constant temperature will be proportional to the bulk concentration c_0. An inspection of our data for the lower concentrations and temperatures shows that Π varies linearly with $t^{1/2}$ up to Π = 7–10 dyn/cm and that the slopes do increase approximately in proportion to c_0. (The best straight lines through the data on plots of Π *vs.* $t^{1/2}$ do not pass through the origin but yield extrapolated values of t = 0.5–2 min at $\Pi = 0$; this may reflect the uncertainty in initial drop formation times already mentioned.)

To permit further analysis of the data, we have calculated the best slopes in the linear Π–$t^{1/2}$ region by least squares for each concentration and temperature, using as many points

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TABLE II

FIT OF EQUATION 3 TO EXPERIMENTAL DATA ON RATE OF SURFACE TENSION LOWERING OF POLYSTYRENE BY STYRENE–DIMETHYLSILOXANE BLOCK COPOLYMER

		Experimental least-squares fit				
Copolymer concn, %	Temp, °C	Slope, a, dyn/(cm min$^{1/2}$)	No. of points	Π_{max}, dyn/cm	D, cm^2/sec	Slope, Figures 2–4
0.05	171	0.93	17	11.4	6.3×10^{-9}	0.84
	185	1.42	13	11.0	1.4×10^{-8}	1.40
	200	2.28	4	8.2	3.5×10^{-8}	2.32
0.1	166	1.23	15	10.9	2.8×10^{-9}	1.31
	185	2.65	8	7.5	1.2×10^{-8}	2.81
	200					4.64
0.2	185					5.62

as appear to fit the linear relationship. Table II gives the values of a, the least-square slope, the number of points used, and the maximum Π value in the linear region.

If eq 3 is valid, the slope may be used to estimate a diffusion constant according to

$$D = \pi a^2/(2RTc_0)^2$$

Expressing the concentrations in moles per cubic centimeter based on the total $\bar{M}_n$ of the block copolymer and the density of the homopolystyrene at the temperature of the experiment yields the values of D in Table II. Figure 5 shows the Arhenius plot of these values; the line corresponds to an activation energy of 5.2 kcal/mol, with $D = 3.6 \times 10^{-8}$ cm^2/sec at 200°. An indication of the fit to the experimental data is provided in Figures 2–4, where the solid lines represent eq 3 with the diffusion constant at each temperature taken as the value obtained from the straight line in Figure 5. (The corresponding slopes are listed in Table II.)

There are few experimental data on diffusion of polymer molecules in melts with which to compare these estimates. Bueche[22] has suggested that for polystyrene the relation

$$D\eta = 4.3 \times 10^{-8} \text{ cgs unit}$$

should hold. The data of Allen and Fox[23] for the viscosity of anionically polymerized polystyrenes then yield estimates of D at 217° of $2.2\text{–}6.3 \times 10^{-9}$ for molecular weights of 5,000–10,000. The value of 9.8×10^{-8} at 217° in our system, obtained from Figure 5, is therefore 10–50-fold larger. While no quantitative interpretation of this difference is possible, the fact that our value is larger than that estimated for homopolystyrene is quite reasonable. This result would be expected because of both the greater mobility of polydimethylsiloxane segments and the larger free volume associated with the copolymer (the experimentally measured specific volume of the copolymer is about 1% greater than would be estimated by averaging those of the homopolymers of similar molecular weights).

While our results cannot conclusively demonstrate the validity of the diffusion-limited adsorption mechanism, they seem entirely consistent with it. It is somewhat surprising that the kinetics appear to be diffusion-limited to such high surface pressures. This may imply that these reductions of surface tension of 7–10 dyn/cm in fact correspond to quite low surface concentrations. The slow change of surface tension over a long period of time in our experiments is then related to the further transition to the substantially pure siloxane surface layer which we have postulated at equilibrium. At present we can offer no quantitative interpretation of this stage of the adsorption process.

Acknowledgment. We are greatly indebted to Dr. J. W. Dean, who kindly provided the block copolymer sample.

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