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# Adsorbed Block Copolymer of Poly(2-vinylpyridine) and Polystyrene Studied by Neutron Reflectivity and Surface Force Techniques

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ABSTRACT: The adsorption of a small block copolymer of poly-(2-vinylypyridine) and polystyrene has been studied as a function of solvency. Both neutron reflectometry and surface force measurements have been used to study the structure of the adsorbed layer. The results show that the adsorbed polymer is highly extended in good solvency conditions for the polystyrene but collapses when the solvent worsens. The results are compared with the self-consistent mean-field theory of Evers–Scheutjens–Fleer for the adsorption of block copolymers. Both the extended length of the polymer and the amount of polymer adsorbed on mica have been measured independently. For this small polymer it is found that both the extended length and the amount adsorbed are about twice as large as would be expected from theoretical predictions based on the size of the blocks but are consistent both with each other and with the neutron data.

## Introduction

In the last few years there has been an increasing interest in the structure of adsorbed block copolymers at interfaces. This interest has arisen in part due to the use of these materials as steric stabilizers and compatibilizers. The advantage of a block copolymer over a homopolymer is that different solubilities and surface affinities can be combined in the same molecule. Their advantage over random copolymers is that one block can be preferentially adsorbed almost to the exclusion of the other and this leads to a more controllable steric barrier. Early results given in a series of papers by Howard et al.[1] indicate that there is very little difference between random copolymers of styrene–2-vinylpyridine (PS–PVP) and block copolymers, though in that study no control of molecular weight was undertaken. They did note, however, that in a preferential solvent only a small proportion of the adsorbing block was required to give a relatively large adsorbed amount and that the adsorption reached a maximum at approximately 18% by weight of PVP. This latter observation is in line with more recent results of Wu et al.[2] and Guzonas et al.[3,4] In the former study, a clear maximum is seen in the plot of adsorbed amount against block copolymer composition for AB blocks of (dimethylamino)ethyl methacrylate (DMAEM) and *n*-butyl methacrylate (NBM) adsorbed on silica from 2-propanol. In that solvent system, the DMAEM block is adsorbed whereas the NBM is not. For the block copolymers of poly(ethylene oxide) and polystyrene (PEO/PS) adsorbed on mica from toluene, a similar trend was noted.[4] In both of these systems the extension of the adsorbed layer into solution has been determined. In the Du Pont work this was achieved using photon correlation spectroscopy and in the XRCC work by using the surface force apparatus (SFA) and determining the onset of repulsion. Both of these experimental methods detect the extremity of the adsorbed layer although the exact definition of the "length" $L$ is slightly different in each case. This length is determined mainly by the tails of the nonadsorbing block and typically the experimental values obtained for $L$ are many times the radius of gyration of the nonadsorbing block in solution.

A more detailed picture of the adsorbed layer can be obtained by using small-angle neutron scattering (SANS)[5–7] and neutron reflectometry (NR)[9,10] techniques. The use of neutrons enables the resolution of structures on a scale of the monomer units of the chain. For block copolymers volume fraction profiles have been obtained by SANS for PEO–PPO–PEO (PPO = poly(propylene oxide)) adsorbed on deuterated polystyrene latex in a contrast matched dispersion medium of water.[5] In that study, the maximum extent of the layer was determined by the length of the PEO tails and was found to scale with molecular weight as $M^{0.55}$. This is just under the scaling prediction exponent of 0.6 found by Taunton et al.[11] for end-terminated polystyrenes. In a more extensive study Auroy et al.[6] found, for terminally attached poly(dimethylsiloxane) chains, a rather good agreement with the Alexander–de Gennes scaling relation of the form

$$L \sim M\sigma^{1/3} \tag{1}$$

where $M$ is molecular weight and $\sigma$ is the surface density. The scaling relations are related when the graft density depends on the radius of gyration of the nonadsorbing block.

In polymer-stabilized nonaqueous dispersions the role of solvency is important in determining colloidal stability. In good solvents at full surface coverage, the presence of the adsorbed polymer layers leads to an effective repulsion between the particles. As the solvency worsens the chains become less repulsive and eventually the system will flocculate. The direct correlation of the critical flocculation temperature and the theta temperature has been debated extensively elsewhere.[12] Similarly the critical role of free volume in this relationship has also been identified.[13] This continuing investigation underlines the importance of understanding the relationship between the force profile

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and the structure of the adsorbed layer in the presence of solvent.

The effect of solvency on the structure of an adsorbed polymer has been studied experimentally by SANS.[14,6] For random copolymers[14] it was found that the layer collapsed as the quality of the solvent was reduced. A similar effect was also seen in the hydrodynamic thickness. The SFA has been used by Marra and Hair[15] to investigate the effects of solvency. In that work block copolymers of PEO–PS were adsorbed onto mica from the nonselective solvent toluene. The adsorbed amounts were such that both the PEO and PS polymers were in semidilute solution with the PEO acting as anchor and the PS as the brush. The toluene was slowly replaced by a heptane–toluene mixture and the length of the extended polymer was measured. It was found that a considerable change in length was induced: A PS brush ($M_w$ = 334K) was found to decrease from 100 nm in pure toluene to about 25 nm at slightly better than $\theta$ conditions. Below $\theta$, the forces became attractive, the chains collapsed and only adhesive contact was obtained. For terminally attached chains the collapse of the volume fraction profile in a nonsolvent has also been detected by nuclear magnetic resonance relaxation[16] experiments.

Because of experimental considerations most of the polymers used in the SFA to determine scaling relationships are larger than are needed to ensure steric protection in colloidal systems. In this paper we investigate the structure of a small block copolymer of PVP and PS adsorbed on a quartz block (neutron reflectivity) and on mica (surface force apparatus) as a function of solvency. The results are compared with some theoretical predictions using the self-consistent mean-field theory of Evers–Scheutjens–Fleer[17] (ESF).

## Experimental Section

The neutron reflectometry experiments were carried out on the CRISP[18] reflectometer at the Rutherford Appleton Laboratory in Oxford, U.K. The details of the sample procedure and cell have already been published elsewhere.[8] A wavelength range of 0.27 to 0.65 nm was used giving an effective $Q$ range of 0.12 to 2 nm$^{-1}$. [$Q = 4\pi \sin(\theta/\lambda)$, where $\theta$ = angle of incidence and $\gamma$ = wavelength of neutrons.] For the experiment using the quartz substrate the neutron beam is passed through the quartz block and is reflected at the solid/solvent interface from the solid side. In this geometry it is possible to contrast match the quartz substrate with the solvent so that only the adsorbed polymer contributes to the observed reflection. This experiment is therefore similar to a SANS experiment at contrast and in principle the data can be numerically transformed[19] to give the volume fraction profile. This is discussed in the following section. The changes in solvent were accomplished by washing out the cell with new solvent. It was assumed, and this was confirmed by the data, that no polymer was desorbed during this process.

The surface force measurements were carried at XRCC, using a surface force apparatus (SFA) which has been described in detail elsewhere.[20] A CCD video camera at the exit slits of the spectrometer was used for computer-aided data collection. The solvents used were all HPLC grade and were dried over molecular sieves and distilled immediately prior to their introduction to the apparatus. Solvent addition and removal were done using a slight pressure of filtered, high-purity nitrogen. The polymer was adsorbed from a 1.5 μg/mL solution of the polymer in toluene, prepared by injection of 3 mL of a stock solution into the surface forces apparatus. After the injection of the polymer, the surfaces were separated to a distance of about 2 mm and allowed to incubate for 3 h, although adsorption appeared to be complete within 1 h. The solvent changes were made with the surfaces close together (<1 μm). Measurements of the force were then made as soon as the apparatus was realigned in the optical path and again at $^1/_2$ h intervals for 2 h. Unless otherwise stated, no differences were observed during this period.

**Table I. Polymer Details**

| polymer | $M_{WA}$ | $M_{WB}$ | $N_A$ | $N_B$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 4–8 | 4000 | 8000 | 39 | 77 | 1.2 |

**Table II. $\chi$ Values for Polymer Solvent Interactions**

| $\chi$ | VP | PS |
|---|---|---|
| VP | 0.0 | 2.0 |
| PS | 2.0 | 0.0 |
| toluene | 2.0 | 0.43 |
| cyclohexane | 2.0 | 0.6 |
| octane | 2.0 | 1.0 |

**Table III. $\chi_s$ Values for Quartz**

| $\chi_S$ | PVP | PS |
|---|---|---|
| all solvents | 2.5 | 0.5 |

The polymer sample was prepared by sequential anionic polymerization and the molecular weight and composition are given in Table I. The polymer was chosen to be slightly asymmetric and will be referred to by the molecular weights in thousands. In this case the polymer is 4/8 and has a $M_w$ of PVP = 4000 ($N$ = 39) and a $M_w$ of PS = 8000 ($N$ = 77). As both segments are protonated they are both visible when the quartz block is contrast matched with the solvent. No correction was made for the differences in neutron scattering length densities for the two blocks.

## Theoretical Modeling

The modeling of the adsorbed block polymer was done using the Evers–Scheutjens–Fleer[17] (ESF) model for adsorption. The various $\chi$ values that have been used are shown in Table II.[21] The $\chi_s$ values used are given in Table III. The strong preferential adsorption of the PVP block is modeled by taking $\chi_s$ equal to −2.5. Although the PS does not adsorb from toluene onto mica, it does adsorb onto silica,[4,5] and hence a value of $\chi_s$ of 0.5 was chosen. This is only just larger than the critical value for adsorption. As both PS and PVP are "stiff" chains, a value of six monomers per lattice site was chosen. This is consistent with the persistence lengths of these polymers, though the direct scaling of the lattice to real space remains problematical.

## Results

The 4-8 polymer has 39 VP segments and 77 PS segments. The adsorbed amount has been estimated directly from the neutron reflectometry experiment as 3.5 mg/m$^2$ and this was confirmed by X-ray reflectometry of the dried film. This value is higher than would be expected from extrapolation of the data given by Tirrell et al.,[22] although it is noted that the substrates are not identical. However, as the PVP block is thought to be strongly preferentially adsorbed, it would be expected that the adsorbed amounts on quartz and mica would be similar and evidence in the literature from ratiotracer measurements[22] on both substrates would tend to support this expectation. In order to further confirm the adsorbed amount Dr. Carl Tripp has independently used the DBFTIR measurement developed at XRCC.[23,24] A value of 3.3 mg/m$^2$ for adsorption on mica is in excellent agreement with the present data and the question of amount adsorbed will be addressed later.

The raw neutron reflectivity data are given in Figure 1. The solid lines are fits to a model in which the PVP segments are described by a block and the PS by a half Gaussian. In order to fit the data a surface roughness has also been introduced. This rounds the block profile both at the substrate side and at the junction between the blocks. The data presented here are for the condition of contrast match between the solution and the substrate. Further

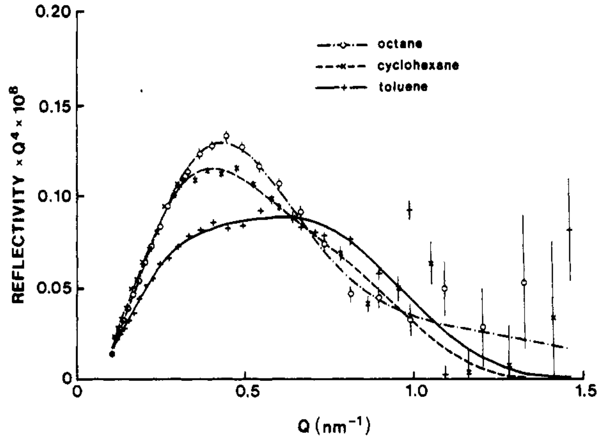

**Figure 1.** Porod plot ($Q^4I$ vs $Q$) for neutron reflectivity data, polymer 4-8 adsorbed on quartz.

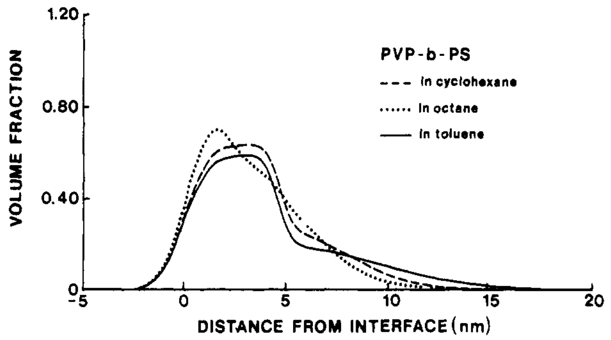

**Figure 2.** Volume fraction profile of polymer 4-8 adsorbed on quartz using data from Figure 1.

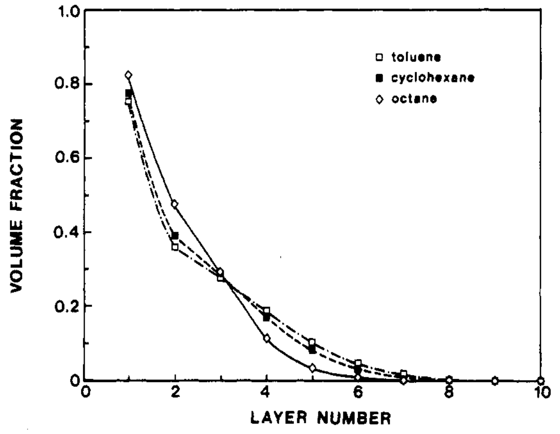

**Figure 3.** Evers–Scheutjens–Fleer model of volume fraction distribution of polymer 4-8 in octane, cyclohexane, and toluene.

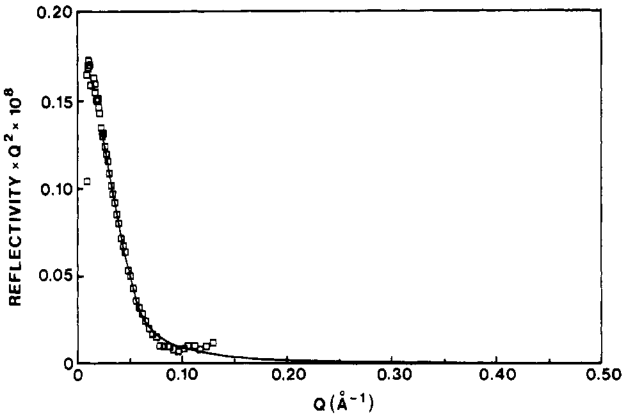

**Figure 4.** Experimental reflectivity data smoothed and extrapolated.

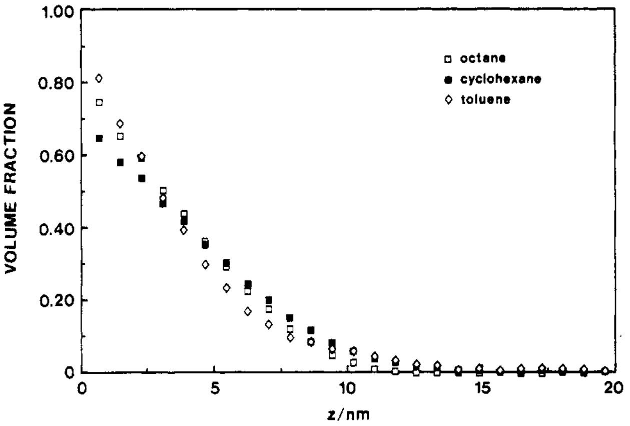

**Figure 5.** Volume fraction curve obtained from extrapolated data in Figure 4.

work on this system[29] has shown that there is a regime near the quartz surface that only becomes visible when the contrast is varied. This surface phase however is unlikely to affect the thickness and extent of the adsorbed layer to any great extent. Figure 1 shows a Porod plot [$Q^4I$ vs $Q$] for the same data and clearly reveals an interference fringe which becomes more pronounced as the solvency becomes worse. These data are rather similar to that obtained for terminally attached poly(dimethylsiloxane) on silica obtained by Auroy et al.[6] using SANS and reflects the compression of the layer on going from a good solvent (toluene) to a nonsolvent (octane). The resultant volume fraction profiles based on a these fits are shown in Figure 2. The volume fraction profiles have several features but most importantly show the expected trend with worsening solvency conditions for the PS block. Figure 3 shows volume fraction profiles for the 4-8 polymer as predicted using the ESF program and the experimental amount adsorbed. The simulation predicts that the volume fraction of segments near the surface is about 0.8. This is similar to the experimental fit which maximizes at about 0.7. The experimental profiles however show a dip toward the surface and this is likely to be due to the fact that the boundary between the quartz surface and solution is not completely planar as was revealed by a contrast match variation as described above. Estimates of the thickness of this boundary zone can be made from the degree of Gaussian smoothing required to fit the NR data on the bare substrate. These results indicate that the surface roughness extends over about 1 to 1.5 nm and would be comparable to several monomer thickness of adsorbed polymer. The extension of the experimentally fitted profiles into the bulk with improved solvency follows the expected order (Figure 2) and this trend is mirrored in the simulation (Figure 3). A concomitant change in the adsorption near to the surface in the simulation is also seen in the experimental data as an increase in volume fraction at about 2 nm.

An alternative way to analyze the reflectivity data at contrast match is to numerically transform the data using the Hilbert transform method introduced by Crowley[19] for small angle neutron scattering when the substrate is at contrast with the solvent. In order to achieve this the raw data must be smoothed and extrapolated and this may reduce the resolution of the inverted profiles. Figure 4 shows the raw reflectivity plotted as $Q^2I(Q)$ vs $Q$ together with the extrapolated and smoothed data. Figure 5 shows the inverted data for the three solvents used as a function of distance $z$ from the interface. As with the fitted profiles the inverted data give a value of the volume fraction at the interface of between 0.7 and 0.8. Comparisons on the extent of the inverted profiles are not clear in this representation and so in Figure 6 the same data are plotted as $1/z$ (nm$^{-1}$). The extents of the profiles can now be estimated more readily and these values are also given in

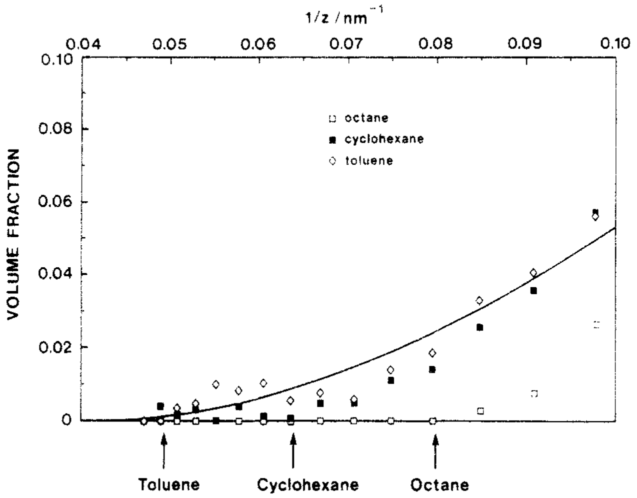

**Figure 6.** Data from Figure 5 plotted against $1/z$ in order to estimate the extension of the profile. Final selected values are indicated by arrows and reported in Table IV.

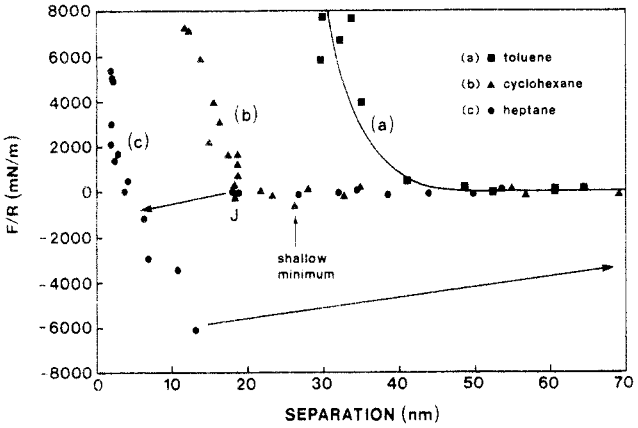

**Figure 7.** Surface force data for polymer 4-8 adsorbed on mica. The arrows represent jumps into contact and out of contact.

**Table IV. Comparison of Layer Extension for 4–8**

| | | neutron data | | |
|---|---|---|---|---|
| solvent | ESF simulation $\delta_{max}$ | $\delta_{max}$ Fit/nm | $\delta_{max}$ Inv/nm | SFA $D_0/2$ |
| toluene | 13 | 16.5 | 20.4 | 20.5 |
| cyclohexane | 11 | 13 | 15.6 | |
| octane | 10 | 12 | 12.5 | |

Table IV. Agreement is good for the nonsolvent case (octane) but there are increasing discrepancies as the solvency is improved and the extrapolation of the tail becomes less accurate.

The extension of the polymer into solution can also be measured using the surface force apparatus. In this experiment the PVP–PS block copolymer is adsorbed onto a cleaved mica surface from a toluene solution. The force curve measured after adsorption is shown in Figure 7a. The interaction is purely repulsive and is first noted when the surfaces are about 41.0 nm apart (i.e., $L_0 = D_0/2 = 20.5$ nm). Continued application of pressure shows that the polymer approaches a "hard wall" configuration at 30.0 nm (i.e., with 15 nm thickness of polymer on each surface). This value for $L$ is in good agreement with the thickness obtained from extrapolating the neutron data but about 50% larger than that obtained from the simulation and can be reconciled with the SF prediction if 1 lattice layer is taken as 2 nm. However the scaling of six monomers/lattice site would suggest a scaling of 1.3 nm/layer; this inconsistency is unresolved but the qualitative picture is encouraging.

When toluene was replaced by cyclohexane (a close-to-$\theta$ solvent), the distance at which interaction is first noted was considerably shortened. When the surfaces were 28.0 nm apart, they experienced a small attractive force which brought them into contact. A "hard wall" repulsion occurs at 11.0 nm. The forces are reproducible, in and out, and reveal a very shallow minimum.

**Table V. Comparison of Scaled Values for $\delta_{max}$ for 4–8**

| solvent | scaling | $\delta_{max}$ Inv | $\delta_{max}$ ESF |
|---|---|---|---|
| toluene | 1.0 | 1.0 | 1.0 |
| cyclohexane | 0.64 | 0.76 | 0.85 |
| octane | 0.31 | 0.61 | 0.77 |

With heptane (a nonsolvent) surrounding the adsorbed polymer, the behavior is similar to that observed in previous studies of block copolymer adsorption. A strong attractive force is noted when the surfaces are 19.0 nm apart and continued compression reveals a "hard wall" layer at 3.8 nm (i.e., 1.9 nm on each surface). The forces are reproducible and an adhesive force of –6.2 N/m is recorded. We note at this point that one method of determining the amount of polymer adsorbed on the mica surface in the SFA has been to adsorb from toluene, collapse the polymer in heptane, and then measure the thickness of the polymer layer below $\theta$. By calibration with PS the amount of blick copolymer adsorbed can be estimated. This refractive index method probably over-estimates the amount adsorbed.[25] Using the method in this case leads to an adsorbed amount of only 1.5 mg/m$^2$—well *below* the amounts measured by neutron adsorption, X-ray scattering, and DBFTIR. It is concluded therefore that collapsed polymer is removed from the surface by the force applied between the plates (see later discussion).

## Discussion

There does not appear to be any detail in the literature regarding the $R_g$ of PVP–PS block copolymers. However, the polymer may be treated as a soluble polystyrene of $M_w = 8000$ ($N = 77$) with an insoluble PVP component. In this case, by use of the values given for PS by Parsonage et al. the $R_g$ may be estimated as $R_{PS} = 1.86 N_{PS}^{0.595}$ (i.e., 2.47 nm). There is some suggestion that low $M_w$ PVP (<4000) may be soluble in toluene. In this case the polymer may more reasonably be treated as a polymer of total $M_w = 12\,000$, i.e., $N = 116$. In this case $R_g = 3.15$ nm.

A comparison of $L$ shows that for the adsorbed block copolymer in toluene the profiles extend to approximately 8 times the solution radius of gyration (good solvent) whereas in octane this is reduced to 6. Although an absolute comparison between the model and the experimental data requires scaling the lattice model to real space, this can be circumvented by normalizing the results to those of toluene. This is shown in Table V. In free solution, polystyrene will scale as $M^{0.6}$, in cyclohexane as $M^{0.5}$, and in octane (assuming a collapsed sphere) as $M^{0.33}$. The ratio of these values to the good solvent using 77 monomers as the polystyrene chain is also shown in Table V. Comparison with the normalized values from the experiment indicate that the chains are not fully collapsed. This is due to the high adsorbed amount which encourages the chains to stretch even in a poor solvent and is qualitatively in agreement with the predictions of Zhulina et al.[26] which suggest that the transition through $\theta$ for an adsorbed polymer is not smooth but occurs over considerable distance. Also, at these low molecular weights some slight solubility is possible.

Another indication of the profile shape is to calculate the second moment $\sigma$ of the distribution of segments about the mean of the profile extent.[7] This can be done from

**Table VI. Comparison of Second Moments for 4–8**

| solvent | $\sigma$/ESF layer | $\sigma$/nm $Q$ data | $\sigma$/nm Fit | $\sigma$/nm Inv |
|---|---|---|---|---|
| toluene | 1.64 | 2.8 ± 0.2 | 2.9 | 3.1 ± 0.2 |
| cyclohexane | 1.46 | 2.6 ± 0.2 | 2.6 | 2.8 ± 0.2 |
| octane | 1.09 | 2.3 ± 0.2 | 2.3 | 2.3 ± 0.2 |

the low $Q$ fit, the inverted profile and the fitted profiles. The results are shown in Table VI. Comparison of these three different ways of obtaining $\sigma$ shows that the inverted data are self-consistent. For a rectangular profile of width $d$ it is known that $d = 12^{0.5}\sigma$. Comparison of the respective values shows that $d$ is much larger than this calculation would predict and that the shape of the profile cannot be mapped as a constant density. The values of $\sigma$ also decrease with reduced solvency.

Although the gross features of these two numerical methods for obtaining the volume fraction profiles are consistent, there are several differences. The details of these will be deferred to a subsequent publication as the features of interest in this work are the thickness and the extent of the layers.

The thickness of the adsorbed layer has been measured for several block copolymers and end-terminated polymers adsorbed on mica. Using data from Taunton et al.[11] the present authors have shown[27] that for end-terminated polystyrenes the length is described by the relation

$$L_0 = 8.89N^{0.6} \qquad (3)$$

Similarly for PEO-*b*-PS polymers, Guzonas et al.[3] have shown that the length is adequately described by the Marques–Joanny relationship

$$L \sim N_{\mathrm{PS}}N_{\mathrm{PEO}}^{-1/3} \qquad (4)$$

The prefactor in this relationship is about 2.5. Using these two equations and the values of $N_{\mathrm{PS}} = 77$, $N_{\mathrm{PVP}} = 39$, and $N_{\mathrm{T}} = 116$, we can derive a value of $L = 154$ Å from eq 3 and $L = 57$ Å from eq 4. These predictions are clearly not in agreement with the SFA and NR measurements reported in this paper. However, we note that the mass of polymer adsorbed in these experiments is accurately determined to be 3.5 mg/m$^2$. This is about twice that recorded in the previous measurements of Parsonage et al.[22] and Boils et al.[25] Returning to the original Alexander[28] relationship, which is the basis for the other derivations, we see that

$$L_0 = Ns^{-2/3}a^{5/3} \qquad (5)$$

where $s$ is the mean spacing between grafting points. From this we note that an increase in the amount of adsorption (for whatever reason) by a factor of 2 would lead to an increase of $2^{1/3}$ (i.e., 1.26) in the length of the polymer. If the 4-8 polymer could be treated as an end-terminated polymer, then this would increase the predicted $L_0$ to 194 Å—in surprising agreement with the experimental results.

It is not clear whether this concept of analogy with end-terminated polymers has any validity. However, it should be remembered that the molecular weights of the two-component polymers are both very low—particularly that of the PVP. There is reason to believe that an oligomer of only 33 VP units would be soluble in toluene[21,22] and this could then not be considered as a selective solvent. That the adsorption of this polymer to the mica is marginal is evidenced by that fact when the polymer is collapsed in heptane the SFA experiments clearly show that at least half of the material is desorbed simply by pressing the two surfaces together. Thus, although a repulsive force is clearly demonstrated (in toluene), it seems unlikely that this polymer would be an effective stabilizer for colloidal particles.

One further item of interest arises from a comparison of the neutron and surface force studies. The segment density profile obtained by NR clearly shows that the segment density distribution exists out to 120 Å even in octane. However, the SFA data in nonsolvent always show an attractive interaction. These results provide a clear demonstration of the importance of the nature of the polymer/solvent/polymer interaction in determining stability rather than a simple consideration of the segment distribution and the extent of the tails.

## Conclusion

SFA and NR data have been obtained for a small block copolymer of PVP-*b*-PS in good solvent (toluene), close-to-$\theta$ solvent (cyclohexane) and nonsolvent (heptane or octane). As expected the segment density profile is compressed as the solvent quality decreases. There is good agreement between the SFA and NR results in toluene and reasonable agreement with ESF simulations. An unusually large amount of block copolymer is adsorbed and this gives rise to a measured length which is much greater than that predicted by simple scaling. This can be rationalized by treating the block copolymer as a soluble, end-terminated polystyrene.

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