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Neutron Reflectivity Studies of Polymers Adsorbed on Mica from Solution

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ABSTRACT: Neutron reflectivity has been used to study the conformation of a block copolymer (polystyrene–poly(2-vinylpyridine)) and a homopolymer (polystyrene) adsorbed on mica from solution. On addition of polymer the reflectivity profile steepens compared with that obtained from the clean mica/solvent interface. The results have been fitted to various theoretical models of the volume fraction profiles of the adsorbed layer. For the homopolymer system, the best fits were obtained with profiles having the form of an exponential decay, whereas for the block copolymer in toluene, profiles with a maximum or a parabolic shape gave the best fits.

Introduction

The structure of adsorbed polymers is of fundamental importance in understanding the mechanisms of steric stability of colloidal dispersions and the role of polymers in a vast number of practical applications ranging from adhesives, to crystal habit modifiers, to cell recognition. The detailed structure of the adsorbed layer can be investigated by a large number of experimental methods.[1] Of these, however, only small-angle neutron scattering (SANS)[2] and evanescent wave methods[3] have been successful in determining directly more than just the first or second moment of the volume fraction profile normal to the interface. SANS in particular has led to the direct determination of the volume fraction profile in systems comprised of stable particulate dispersions with high interfacial areas. There is considerable interest in the structure of polymers on flat macroscopic surfaces, arising in part from the large body of data obtained from force-balance measurements between polymer-coated mica surfaces.[4-6] With regard to the thickness of an adsorbed layer on a free surface, this technique gives an indication of the maximum extent of the adsorbed layer, which can be determined from the surface separation at which a force is first detected. The force–distance profiles themselves have been successfully interpreted by using both scaling theory and mean-field predictions of the structure of the adsorbed layer. However, SANS data[1,2,7] give no indication that at the chain lengths studied to date (~22 000 monomers of poly(ethylene oxide) (PEO)) that the volume fraction profile, $\varphi(z)$, follows a simple scaling law. Indeed the experimental profiles obtained show a pronounced curvature over the entire double-logarithmic plot.[2] Other SANS data,[8] however, indicate that, for a more flexible chain (poly(dimethylsiloxane)), some agreement with the scaling prediction is plausible. The thickness of polymer layers on macroscopically flat surfaces has also been extensively studied by ellipsometry[9] and capillary flow,[10] though again in both these methods only the average thickness of the polymer layer can be obtained.

The SANS method is restricted in its applicability not only in that the samples must be particulate and of the order of 100–500-nm diameter but also in that these dispersions must be stable. This means that nonaqueous dispersions below full polymer coverage cannot be reliably investigated if flocculation occurs. Some of these limitations could in principle be overcome by using neutron reflectivity.

In this paper we report the application of neutron reflectivity to studying the structure of a polymer layer adsorbed from solution and in the presence of a liquid film of solvent. The results are compared with calculated reflectivity based on theories of polymer adsorption.

Experimental Section

Materials. The mica sheet was obtained from Mica and Micanite Supplies Ltd. and was freshly cleaved to provide a clean surface. Deuterated polystyrene (DPS) (Polymer Laboratories, Ltd., Church Stretton, U.K.) and a block copolymer of deuterated polystyrene and poly(2-vinylpyridine) (DPS–PVP) were studied. The copolymer was prepared in this laboratory by sequential anionic polymerization. Details of these polymers are given in Table I. The analytical grade solvents and their deuterated analogues were obtained from Aldrich Chemical Co.

Procedures. The CRISP[11] reflectometer at the Rutherford Appleton Laboratory in Oxfordshire was used to study the two polymers adsorbed from solution onto mica. A supermirror was used in the incident beam to bring it to shallower angles than its normal 1.5° to the horizontal. The glancing angles of incidence (θ) of 0.35° and 0.55° were used. A useful wavelength range of 2.7–6.5 Å was obtained, giving an overall range in Q ($4\pi \sin \theta/\lambda$) of 0.012–0.045 Å^{-1}. The geometry of the reflectivity experiment required a mica substrate of ~4 × 15 cm in order to use the full beam and hence maximize the number of neutrons reflected. The sample was placed in a stainless steel, sealed enclosure and supported on a rack such that the sample could be held as flat as possible. All experiments were performed at room temperature. The enclosure was made with mica windows at each end in order to transmit the beam. The sample was aligned at the correct orientation by means of a laser beam that is collinear with the neutron beam. This alignment procedure proved problematic, given that the surface of mica is not macroscopically completely flat and that there is a variation in this between samples. The surface, however, is virtually atomically smooth, save for a few steps introduced by the cleavage operation. Due to the difficulty of alignment the solvent and then the polymer solutions were added to the substrate in situ.

The thickness of the liquid layer was not controlled directly. However, it could be maintained within acceptable limits (i.e., not too thin to affect the polymer conformation and not too thick to attenuate the beam completely) by having excess solvent in the bottom of the enclosure so as to saturate the atmosphere and prevent evaporational loss. The thickness of the layer was monitored continually during the experiment by observing the reflectivity close to the critical edge, using an incident angle of 0.35°. The linear attenuation coefficient of cyclohexane was measured in a separate experiment by direct transmission from 0.5 to 6.5 Å and was found to be 0.415 mm^{-1} and independent of wavelength over this range. This meant in principle that the thickness of the layer could be estimated. The mica was sufficiently thick to eliminate scattering from its lower surface.

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Table I
Polymer Sample Details

sample	M_n	M_w/M_n
50k DPS	49500	1.05
DPS-PVP		
DPS block	15000	1.2
PVP block	500	

Table II
Adsorbed Amounts from Dried Samples

sample	thickness/Å	adsorbed amount/(mg m^{-2})
mica/DPS	33 ± 5	1.1 ± 0.5
mica/DPS-PVP	44 ± 3	2.9 ± 0.5

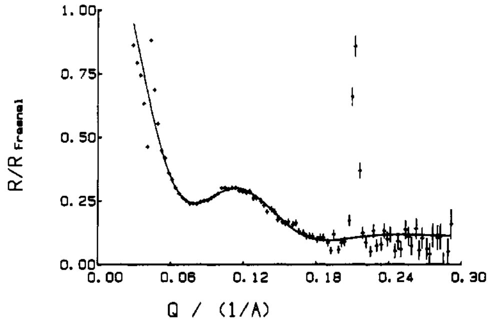

Figure 1. X-ray film factor for dried DPS-PVP sample on mica: (+) data; (—) fit.

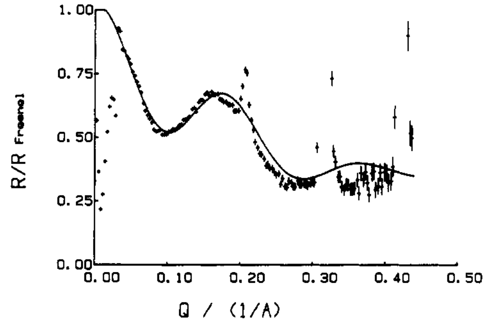

Figure 2. X-ray film factor for dried DPS sample on mica: (+) data; (—) fit.

The solvents used were toluene and a mixture of 4% perdeuterated and 96% hydrogenous cyclohexane. The cyclohexane mixture has a neutron scattering length density of zero, equal to that of air ("contrast matched").

Adsorption experiments were carried out by adding an excess of polymer solution directly onto the substrate. The polymer solution concentrations used were of the order of 1000 ppm by mass. The adsorption of the copolymer is essentially irreversible, and excess polymer in solution was removed by washing with an excess of solvent. This was necessary in order to preclude any contribution to the reflectivity from polymer adsorbed at the liquid/air interface. For the polystyrene homopolymer this may lead to some desorption, though Terashima[12] has found the proportion of polymer desorbed is small. Adsorbed amounts were estimated by X-ray reflection[13] from the dried samples after the neutron experiment. This was done by assuming that the polymer had dried to a compact layer whose thickness and electron density were determined. In order to fit the data, however, it had to be assumed that an incomplete layer was formed on drying that covered $\sim$60% (DPS) and $\sim$86% (DPS-PVP) of the mica surface. Details of the adsorbed amounts calculated from the X-ray and neutron data are given in Table II. Both the average thickness and the incomplete nature of the dried layer support the fact that the DPS adsorbs to a considerably less extent than the DPS-PVP. The "film factors"[13] obtained by dividing the samples' X-ray reflectivities by that from a sharp interface are shown in Figures 1 and 2.

Table III
Volume Fraction Profile Details

profile	equation/parameters
SF(tail)	terminally attached, $\chi = 0.45$, $\chi_s = 0.0$, $r = 30$, $\Gamma = 2.9$ segments/surface site; $\varphi_{max} = 0.45$ from simulation
SF(phys)	physical adsorption, $\chi = 0.5$, $\chi_s = 1.0$, $r = 100$, equilibrium polymer concentration = 1000 ppm, $\Gamma = 1.3$ segments/surface site; $\varphi_{max} = 0.64$ from simulation
exponential	$\varphi(z) = \varphi_{max} \exp(-z/z_0)$
Gaussian	$\varphi(z) = \varphi_{max} \exp\{-([z/z_0] - \delta)^2\}$
parabola	$\varphi(z) = \varphi_{max}({z_0}^2 - z^2)$

Analysis of Reflectivity Data. The neutron reflectivity of each sample was analyzed by fitting a selection of theoretical scattering length density profiles to the data, using a program based upon the Harwell nonlinear least-squares fitting routine VA05A.[14] The profiles used were an exponential decay, a parabolic decay, a shifted Gaussian, and two profiles (SF(phys) and SF(tail)) calculated from the mean-field theory of Scheutjens and Fleer.[15] The scattering length density of the polymer in solution is divided by the scattering length density of the bulk polymer to obtain the volume fraction (φ). The reflectivities from the model scattering length density profiles were calculated by using a matrix method based upon Fresnel reflection coefficients.[16] Each profile is broken up into 24 increments to simulate the smoothly changing density profile of the polymer and has two variable parameters; these are the maximum scattering length density of the profile and the width of the increments. For the shifted Gaussian profile there is a third parameter, δ, which defines the position of the peak maximum relative to the mica surface. When $\delta = 0$ the maximum occurs at the mica surface and when δ is positive it is shifted away from the surface on the solution side. When $\delta = (\ln 2)^{1/2}$ the surface meets the peak at half-height. Table III gives details of the profiles; for the analytical functions the width of the increments is altered by varying the value of the parameter z_0. For the SF models one increment corresponds to one lattice layer. The relative heights of the increments are thus determined by the profile shape being fitted, and so the characteristic shape of the profile is maintained throughout the fitting procedure. However, since the adsorbed amounts are known approximately (and correspond to the area under the profiles), only the widths of the increments (and for the shifted Gaussian, the value of δ) are freely variable and the value of φ_{max} is chosen to keep the adsorbed amount constant. Thus for each value of the adsorbed amount there is only one degree of freedom in the fitting procedure (two in the case of the Gaussian).

The quality of each fit can be assessed visually and also by the calculated "χ^2" parameter from the least-squares fitting routine. The latter approach is not entirely satisfactory since the error bars are calculated only for neutron counting statistics. For data around the critical edge the count rate is sufficiently high for systematic errors from either the instrument or, more probably, the nonplanarity of the sample to be more significant than the purely statistical errors. This can lead to rather high values of χ^2, although the relative values of χ^2 of different fits to the same data set are still a good indication of their relative quality.

Results and Discussion

(1) Block Copolymer Adsorption. Figure 3 shows reflectivity data obtained from the bare mica substrate and mica with the addition of the contrast-matched cyclohexane. The data have been scaled to unit reflectivity below the critical edge so that they can be superimposed. Within experimental error the upper surface is essentially "invisible". In order to fit the data for bare mica an air/mica roughness does not have to be included, and this confirms that the surface is molecularly smooth to within the resolution of the instrument, i.e., within 5 Å. Figure 4 compares the reflectivity obtained from the bare sample with that from the same sample with added block copolymer solution in cyclohexane. Comparison of a sequence of runs taken while the liquid layer was thinning suggests that the polymer layer is unaffected by the solvent

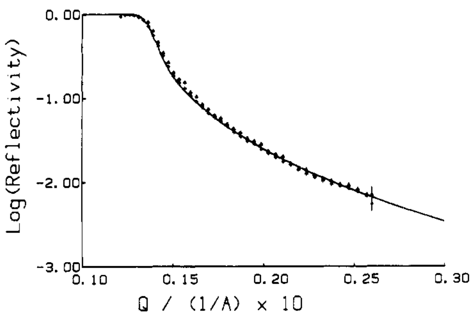

Figure 3. Reflectivity of bare mica and mica/cyclohexane: (+) bare mica; (▲) mica and cyclohexane; (—) fit to single-interface model.

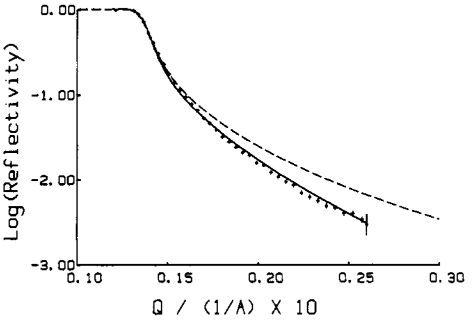

Figure 4. Reflectivity of mica/DPS-PVP in cyclohexane: (+) mica/DPS-PVP in cyclohexane; (—) exponential fit; (- - -) bare mica.

layer thickness. This also supports the assumption that all the polymer in solution was removed by the washing and that no polymer remains adsorbed at the liquid/air interface. The thinning rate at first is very fast as saturation of the vapor occurs and then slows down to give a film of nearly constant thickness. The data have therefore been combined for a series of runs taken at different times. The observed reflectivity is primarily due to the DPS block, which is at strong contrast to the mainly protonated solvent (cyclohexane), whereas the short PVP block is at weak contrast. As cyclohexane is a nonsolvent for PVP, it is likely that these segments will be adsorbed virtually completely and irreversibly.[6] Subsequent measurements taken after drying out the sample gave a reflectivity very close to that from the original mica, showing that indeed the reflectivity was sensitive to the structure of the diffuse layer of polymer solvated at the interface. The dried layer thickness was obtained from the X-ray reflectivity data and found to be $\simeq$40 Å. Its electron density suggested that for neutron reflectivity the scattering length density of a dried-out film would be closely matched to that of mica. This coincidence explains why the dried-out film could not be seen in the neutron experiment. An approximate value for the thickness of the diffuse polymer layer can be estimated from the low-Q data by fitting different models and was found to be of the order of 40 Å. However, it was found that the range of Q was not sufficient to differentiate between different models of the adsorbed layer. A typical fit using an exponential profile is shown in Figure 4, but various other models give essentially the same quality of fit over this limited range in Q.

A similar set of experiments was carried out for the same copolymer under toluene over a larger range in Q. This sample was prepared by washing the mica after adsorption from cyclohexane with the new solvent. There is, however, a complication with the toluene system in that it is not possible to contrast match toluene with air. The results have therefore been taken in pure, hydrogenous toluene.

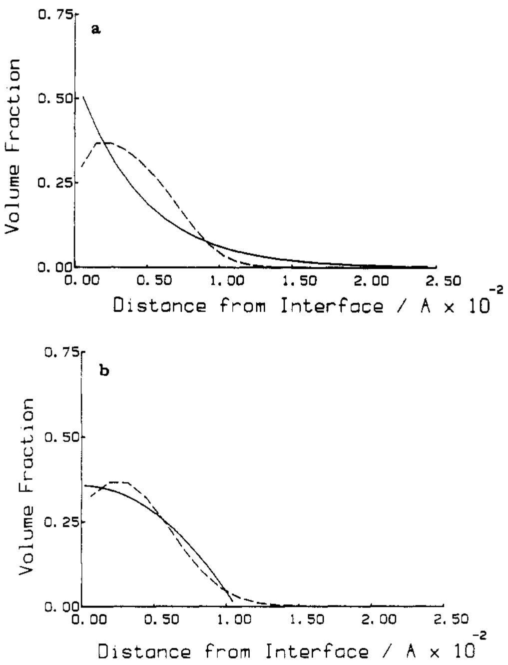

Figure 5. Volume fraction profiles used in fitting procedure (DPS-PVP in toluene, $\Gamma = 2.9$ mg m^{-2}): (a) (- - -) SF(tail), (—) exponential; (b) (- - -) shifted Gaussian, (—) parabola.

The effect of this is that the reflectivity data taken while the layer is thinning rapidly are not superimposable. However, during the slow thinning the change in attenuation in the liquid layer is negligible so that data may be collected over a more extended time. The effect of the incompletely matched toluene/air interface has been accounted for by assuming that the liquid layer is sufficiently thick for there to be no phase coherence between neutrons reflected from the liquid/air and liquid/mica interfaces (reflectivities R_1 and R_2, respectively). The reflected intensities are then calculated separately, and the overall reflectivity is given by the formula

$$R_{\text{total}} = \frac{R_1 + R_2 \exp(-2\beta \sin \theta t) - 2R_1R_2 \exp(-2\beta \sin \theta t)}{1 - R_1R_2 \exp(-2\beta \sin \theta t)}$$

where β is the attenuation coefficient of the liquid. This equation accounts for both attenuation in the liquid (thickness t) and multiple reflection. A higher Q range was measured during the slow thinning period by altering the incident angle to 0.55°. The Q ranges at the two angles overlap somewhat, and this allows the reflectivity at the second angle to be correctly scaled to the first. The combined data for this sample are shown in Figure 6. The effect of the adsorbed polymer on reflectivity is similar to that in the cyclohexane experiment although the effect is more pronounced for this solvent.

In toluene the PVP segments are expected to remain strongly adsorbed, whereas the polystyrene segments are nonadsorbing. The volume fraction profile in this instance should have a pronounced maximum at a distance from the surface of the order of R_g^0, the radius of gyration of the free polymer in solution. This system is similar to that of a terminally attached polymer in a good solvent with a nonadsorbing substrate. SANS studies on such systems, for example, PEO on a nonadsorbing DPS latex in water[17] and DPS on surface-modified silica,[7] have given profiles with a clearly defined maximum some distance away from the surface; this behavior is predicted by the Scheutjens–Fleer (SF) model[15,18] and by a multichain Monte Carlo (MMC) simulation[19] at the surface coverages pertaining to the present experiments. At higher coverages both the

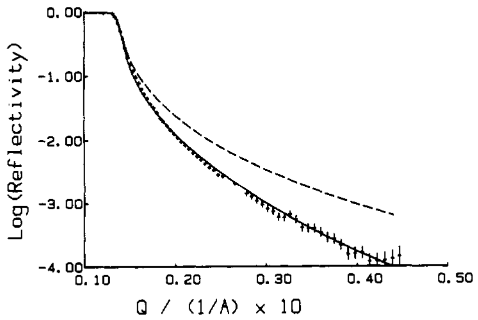

Figure 6. Reflectivity of mica/DPS-PVP in toluene: (+) mica/DPS-PVP in toluene; (—) SF(tail) fit, $\Gamma = 2.9$ mg m^{-2}; (- - -) bare mica.

SF and the MMC models show that the maximum is moved very close to the surface, which is in good agreement with the mean-field analytical model of Milner, Witten, and Cates,[20] which predicts a parabolic form for the profile.

The volume fraction profiles used in fitting these data are shown in Figure 5. For the SF profile (SF(tail)) the Flory-Huggins parameters for the solvent (χ) and surface (χ_s) as well as the adsorbed amount are shown in Table III. These parameters have been chosen to reflect the known properties of the components. The lattice used in the SF simulation is hexagonally closed packed, and the choice of chain length has been based on the known rigidity of the polystyrene chain; this suggests a ratio of between 6 and 10 for the scaling of a real monomer to a lattice spacing.[21] The rms thickness is calculated as $\{\int_0^\infty \varphi(z) z^2\, dz / \int_0^\infty \varphi(z)\, dz\}^{1/2}$. For the copolymer in toluene the shifted Gaussian, SF(tail), and the parabola give equally good fits and the lowest values of χ^2 for Γ in the range 2.6-2.9 mg m^{-2} suggested by the X-ray data. All these fitted profiles have the same rms thickness and are similar in shape; the Gaussian and SF profiles are virtually superimposable. The value of $\varphi_{\max}$ for the SF profile is changed only slightly by the fitting procedure, and the lattice spacing is 10 Å. From this value the real volume of a lattice cell is calculated, and hence the number of real monomers in an occupied cell is then obtained from the known density of the bulk material and found to be 7.5. From this calculation we also obtain the conversion factor from adsorbed segments per surface site to mg m^{-2}; for a lattice spacing of 10 Å this is approximately unity. The calculated reflectivity from the SF profile is shown in Figure 6. Previous SANS data[7,17,21] on similar systems and the adsorbed amounts in this system suggest that there will be a depletion of segments near the interface, giving a maximum in the profile some distance away from the surface. The shape of the profile beyond the maximum, however, has a similar curvature to that of the parabolic form. For comparison it can be seen that the exponential fit to these data is poor, as expected. The derived parameters for these various fits are given in Table IV. The values for the rms thickness can be compared with the unperturbed radius of gyration (R_g^0) of the polystyrene block in solution (36 Å). The exponential profile gives an rms value that is much larger than R_g^0, whereas the other three profiles (SF(tail), Gaussian, and parabola) give closer values. From the curves in Figure 5, which are the actual forms of the profiles resulting from these fits, it can be seen that the poorer fitting exponential profile extends further into solution. The maximum volume fractions (Table IV) are all comparable and are a similar value to that found by SANS studies for terminally grafted DPS on silica.[7,21]

Table IV
Fit Parameters for Polymer/Mica Data

sample	function type	$\varphi_{\max}$	D(rms)/ Å	Γ/ (mg m^{-2})	χ^2
15k DPS-PVP (toluene)	SF(tail)	0.37	48	2.9	5.7
	Gaussian ($\delta = 0.49$)	0.37	48	2.9	5.7
	exponential	0.57	62	2.9	11.5
	parabola	0.37	48	2.9	5.5
	SF(tail)	0.35	46	2.6	5.6
	Gaussian ($\delta = 0.73$)	0.37	45	2.6	5.6
	exponential	0.53	59	2.6	10.6
	parabola	0.38	44	2.6	7.4
50k DPS (cyclohexane)	SF(phys)	0.14	103	1.3	0.92
	Gaussian ($\delta = -0.99$)	0.15	87	1.3	0.76
	exponential	0.17	90	1.3	1.3
	parabola	0.10	75	1.3	5.1
	SF(phys)	0.14	85	1.0	4.8
	Gaussian ($\delta = 0.5$)	0.09	66	1.0	1.1
	exponential	0.17	72	1.0	6.2
	parabola	0.09	63	1.0	1.4

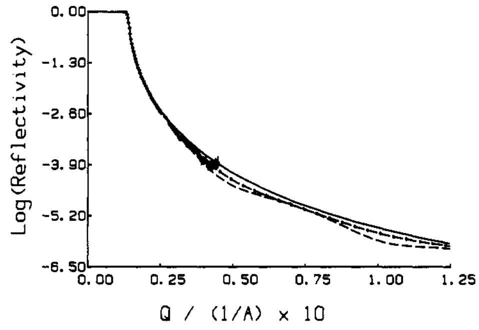

Figure 7. Fitted profiles extended to higher Q, $\Gamma = 2.9$ mg m^{-2}: (- - -) parabola; (—) exponential; (-•) SF(tail).

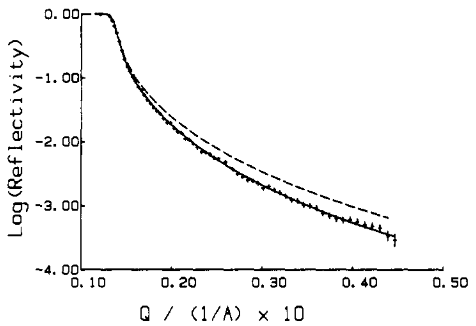

Figure 8. Reflectivity of mica/DPS in cyclohexane: (+) mica/DPS in cyclohexane; (—) exponential fit, $\Gamma = 1.3$ mg m^{-2}; (- - -) bare mica.

It is clear that data over a more extended range in Q are needed to give a less ambiguous measurement of the volume fraction profile; Figure 7 shows extrapolations of the fitted profiles to higher Q which indicates that reflectivity data are sensitive enough to distinguish finer details of the profiles.

(2) Homopolymer Adsorption. Data for polystyrene adsorbed from cyclohexane were obtained over the two overlapping ranges of Q and the data scaled accordingly. The results are shown in Figure 8. The SF profile used in this case (SF(phys)) is for a physically adsorbed homopolymer; the values of χ and χ_s are shown in Table III. The SF model predicts a monotonically decreasing profile (for favorable segmental adsorption energies) which has been confirmed by previous experimental work using SANS to investigate PEO on adsorbing DPS latex in water.[17,21] The best fit to the present data using $\Gamma = 1.3$ mg m^{-2} is consistent with such a profile shape. Note that the Gaussian also shows a good fit but that the value of δ is negative

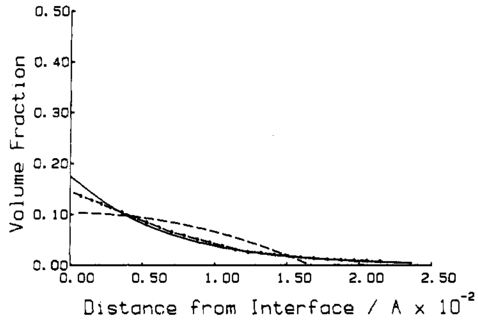

Figure 9. Fitted profiles to mica/DPS in cyclohexane for Γ = 1.3 mg m^{-2}: (- - -) parabola; (-•) SF(phys); (—) exponential.

so there is no maximum in the profile above the surface and the curvature is similar to the exponential. Figure 9 shows the two monotonically decaying profiles, which give the best fits, and also the parabola, which does not fit the data so well. If Γ is set to 1.0 mg m^{-2}, then the χ^2 values are comparable but the best fits now correspond to different profiles. This changeover illustrates both that the adsorbed amount is a very important parameter in constraining the model fitting and that for any given adsorbed amount the maximum decrease in reflectivity obtainable is smaller for exponential-type decays. When constrained to 1.0 mg m^{-2} the exponential and SF profiles cannot produce as large a change in reflectivity as is observed and thus do not fit these data very well. At such low adsorbed amounts it becomes difficult to distinguish between different profiles since the effect on reflectivity is rather weak. However, all the fitted profiles give a low value for φ_{max} and an rms thickness comparable with R_g^0 (68 Å). It should be noted that φ_{max} from the SF prediction is much higher than the values that best fit the data; such a high value for φ_{max} does not fit the data at all. Altering the number of statistical segments in the chain or the χ_s parameter in the SF calculation does not lead to as low a φ_{max} as is observed. If the adsorbed amount is allowed to vary during the fitting procedure, the same profile is obtained as when it is fixed at 1.3 mg m^{-2}. It thus appears that, although the SF theory is predicting approximately the same adsorbed amount as is observed, it overestimates the volume fraction at the surface and underestimates the extent of the tails. It is clear that with a limited range in Q considerable care is needed in making this fitting procedure objective, and it is essential to use complementary data, such as SANS.

Conclusion

Neutron reflectivity data for polymers adsorbed from solution onto mica have been obtained. The results show that the reflectivity is sensitive to the structure of the diffuse adsorbed layer. Comparison with theoretical models of the volume fraction profile of polymers is promising. The present data indicate that (i) physically adsorbed polymers have profiles that decay monotonically but that (ii) adsorbed polymers where the tails are essentially terminally attached and precluded from returning to the interface have profiles that have a maximum or are parabolic. Although the SF theory is quite successful in fitting the observed reflectivity for the copolymer data (essentially terminally grafted), the fit for the homopolymer, although qualitatively reasonable, is quantitatively in error. Clearly, more extensive data are needed to make a more detailed comparison between theory and experiment, and we plan to make such measurements in the future.

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