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Surface phase separation in an amphiphilic block copolymer monolayer at the air–water interface

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Deuterium labelled linear diblock copolymers of polyethylene oxide and polymethyl methacrylate were spread at the air–water interface and neutron reflectometry was used to determine the spatial organization of the copolymer. The mole fraction composition of the block copolymer was *ca* 0.5, but with some variation from copolymer to copolymer arising from the separate syntheses needed for each labelled copolymer. The neutron reflectometry data for two surface concentrations of the block copolymer (0.6 and 1.2 mg m^{-2}) were analysed using the kinematic approximation. In addition to providing the composition and thickness of regions which are rich in one component or the other, this method also gives the separation between each of these regions. For the lowest surface concentration used the two blocks were mixed together near the surface with a Gaussian distribution of segments, the characteristic dimension of which was circa 8 Å. At the higher surface concentration of 1.2 mg m^{-2}, there is a clear separation between the two blocks with the polyethylene oxide exploring the aqueous subphase and part of the polymethyl methacrylate block being expelled into the air phase. However, there is no evidence for the formation of a stretched brush like layer of polyethylene oxide at the surface. Attempts to analyse for such a layer are discussed and the care needed in such analyses is pointed out. For both concentrations the near surface distribution of water takes on a tanh distribution.

(Keywords: copolymer; interface; reflectometry; organization)

INTRODUCTION

Polymers at interfaces play an important role in many applications. At solid–liquid interfaces and liquid–liquid interfaces they often act as stabilizers of colloid dispersions, either as solid particles or emulsions[1]. At vapour–liquid interfaces, polymers may act as anti-foaming agents or be deliberately spread in the process of making thin film devices. The behaviour of polymers particularly at the air–water interface, is mainly inferred from their surface pressure isotherms. Direct information as to the structural organization of polymers at the air–water interface is much more difficult to obtain.

A major focus of attention for polymers at interfaces has been the evaluation of current theories[2–4] concerning the formation of brush like layers and the dependence of layer thickness on grafting density, i.e. the number of polymer molecules attached by an end per unit area of interface. Using small angle neutron scattering (SANS) and porous silica materials, Auroy *et al.*[5] have attempted to obtain the necessary data. However, the grafting density in such systems is not easily controlled, and consequently there have been some attempts made using polymers spread at the air–liquid interface. The grafting density for such spread layers is easy to control, in principle, merely by altering the surface concentration of the polymer. Generally, such investigations utilize linear diblock copolymers, where one block is insoluble and acts as an anchor at the air–liquid interface, and the second block is solvated and behaves as a buoy.

Perhaps the only system where incontrovertible organizational information on brush forming layers has been obtained thus far is the linear diblock copolymer of polydimethyl siloxane and polystyrene spread on ethyl benzoate[6–8]. The polystyrene block dissolves in the ethyl benzoate subphase and since it has a higher surface tension than the subphase it does not form a surface excess layer in close proximity to the interface. However, even with this combination it was noted that there was some slow dissolution of the copolymer into the subphase. Water is by far the most common fluid phase on which polymers are spread and because of the high surface tension of water most water soluble polymers will remain close to the air–water interface and the prospects for observing a significant increase in layer thickness on increasing the surface concentration are reduced. Notwithstanding the confinement of polymers at the air–water interface to the very near surface,

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unique results have been obtained. For example, polyethylene oxide homopolymer when spread at the air–water interface does not penetrate the aqueous subphase until the surface concentration exceeds $\sim$0.4 mg m^{-2}[9]. This conclusion was obtained from neutron reflectometry data and correlated well with an abrupt change in the relaxation time of the spread film obtained from surface quasi-elastic light scattering[10]. An earlier paper[11] discussed the organization of a linear diblock copolymer at the air–water interface where each block was separately deuterium labelled and a highly detailed description of the organization of the polymer was obtained. Surprisingly, there was little variation of the organization of the copolymer over the three surface concentrations studied ($\sim$1.0, 1.5 and 2.0 mg m^{-2}). However, subsequent surface quasi-elastic light scattering experiments[12] indicated the existence of a phase transition in the spread film, notably an abrupt transition in the relaxation time of the spread film (*Figure 1*). We report here the application of neutron reflectometry to the spread copolymer film at two surface concentrations above and below the transition point in *Figure 1*. We apply the kinematic approximation to neutron reflectometry data on partially deuterium labelled copolymers and this approach is outlined below.

THEORY

Detailed theory of neutron reflectometry has been expounded for both the exact optical matrix treatment and the kinematic approximation[13]. We present only an outline of the kinematic approximation here sufficient to appreciate the subsequent analysis of the data. We consider the surface film of spread polymer to have three components, methyl methacrylate block (m), ethylene oxide block (e) and subphase molecules (s). In the kinematic approximation the reflectivity of a neutron beam from the surface film as a function of momentum transfer normal to the surface, Q, ($Q = |\mathbf{Q}| = (4\pi/\lambda)\sin\theta$, θ is the glancing incident angle), is given by

$$R(Q) = \frac{16\pi^2}{Q^2}\begin{bmatrix} b_m^2 h_{mm}(Q) + b_e^2 h_{ee}(Q) + b_s^2 h_{ss}(Q) \\ +2b_m b_e h_{me}(Q) + 2b_m b_s h_{ms}(Q) \\ +2b_e b_s h_{es}(Q) \end{bmatrix} \qquad (1)$$

Where b_i is the coherent scattering length of species i and $h_{ii}(Q)$ and $h_{ij}(Q)$ are self and cross partial structure factors. Self partial factors describe the number density distribution of the species normal to the interface and contain information on the spatial dimensions occupied by the species i and their concentration. The cross partial structure factors contain information about the separation between the individual species i and are expressible in terms of the relevant self partial structure factors (*vide infra*).

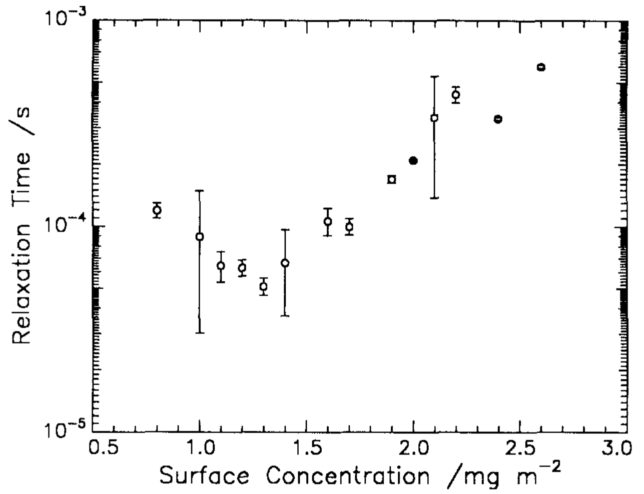

Figure 1 Relaxation times obtained by surface quasi-elastic light scattering of the spread block copolymer film as a function of surface concentration

To obtain all the partial structure factors requires at least six different values of $R(Q)$ under the same conditions of surface concentration and temperature, equation (1) can then be solved for each of the partial structure factors. To obtain sufficiently different values of $R(Q)$ means that full advantage of deuteration should be used. Hence to obtain $h_{ee}(Q)$, the e part of the block copolymer should be deuterated. It is *not* sufficient to adjust relative contrasts by altering (say) the D_2O content of the subphase. For low molecular weight surfactants this technique has been used with great effect[14,15] and highly detailed descriptions of the arrangement of non-ionic surfactants at the air–water interface have been obtained. However, for copolymers of high molecular weight the situation is not as simple. Unless the polymerization process is extremely well behaved there will always be a distribution in molecular weight *and* composition between specimens prepared by separate polymerizations. These possible variations between the differently deuterium labelled specimens will introduce slight differences in the individual partial structure factors. Consequently, the resultant description may not be as definitive as for low molecular weight materials, but should nonetheless provide a better one than available hitherto.

EXPERIMENTAL

Block copolymers

The block copolymers of polymethyl methacrylate and polyethylene oxide were identical to those used earlier[11] except that the copolymer with the deuterated ethylene

Table 1 Molecular weights, compositions and methacrylate block tacticity of block copolymers

				Triad tacticity		
Copolymer	Mole fraction ethylene oxide	$\bar{M}_w$ (10^3 g mol^{-1})	$\bar{M}_n$ (10^3 g mol^{-1})	Iso	Hetero	Syndio
DMDE	0.51	45.4	25.6	0	0.51	0.49
HMHE	0.65	67.3	32.1	0.08	0.54	0.37
DMHE	0.50	62.8	43.5	0.06	0.55	0.39
HMDE	0.70	45.5	19.3	0	0.35	0.65

oxide block was replaced by a newly synthesized (by anionic methods) version. *Table 1* gives the molecular weights of each block copolymer used, the polyethylene oxide content and the tacticity of the methacrylate blocks. Molecular weights were obtained by size exclusion chromatography, compositions and tacticity of each block copolymer were obtained from ^{13}C nuclear magnetic resonance (n.m.r.) spectra of deutero-chloroform solutions of the copolymer.

Neutron reflectometry

Neutron reflectometry data were obtained using the CRISP reflectometer located at the UK pulsed neutron source, ISIS, in the Rutherford Appleton Laboratory, Didcot, Oxfordshire. A rectangular NIMA Langmuir trough (NIMA Technology, Warwick Science Park, Coventry, UK) was placed in the neutron beam and filled with appropriate subphase, either NRW (null reflecting water) or D_2O. NRW signifies that mixture of H_2O and D_2O which has zero scattering length density and which does not reflect a beam of neutrons. The surface was aspirated and swept until the surface tension of clean water was obtained. At this point the necessary volume of copolymer in chloroform solution ($\sim 1\,g\,l^{-1}$) was deposited on the aqueous subphase surface to achieve the desired surface concentration (Γ_s) with the Langmuir trough barriers set at their largest area.

The wavelength distribution of the neutron beam incident on the sample was from 0.5 to 6.5 Å and two angles of incidence of this beam on the liquid surface were used, 0.8° and 1.5° respectively. Reflectometry profiles collected at these two separate angles were combined for each copolymer/subphase composition used, the total range of momentum transfer (Q) covered was $0.026 \leq Q/\text{Å}^{-1} \leq 0.65$. The resolution in Q was 4% over the whole Q range covered and the specularly reflected neutron beam was detected by time of flight methods. All reflectometry profiles were collected at a temperature of 295 K. The flat background arising from incoherent scattering and any small angle scattering was calculated as the average reflectivity over the Q range 0.5 to 0.65 Å^{-1}, this average value was subtracted from the reflectivity values obtained. This procedure has been applied in the past to surfactant systems, polymer solutions and spread layers at air–water interfaces, and is generally accepted as the most appropriate method when time-of-flight detectors are used. Although positive values of the background subtracted reflectivities are obtained for Q values up to *ca* 0.5 Å^{-1}, the error bars for Q values greater than circa 0.25 Å^{-1} are large and reflectivities in this range have not been used in the subsequent analysis using the kinematic approximation.

RESULTS

Figure 2 shows the surface pressure isotherms for the DMDE and HMHE copolymers obtained at 298 K obtained using a Wilhelmy plate and compression of a film spread over an area of 900 cm^2 at a rate of 30 $cm^2\,min^{-1}$. (D = deutero, H = hydrogenous, M = methyl methacrylate, E = ethylene oxide.) The small differences between the two isotherms are attributable to the difference in polyethylene oxide content of the two block copolymers. However, both copolymers show the same features in their isotherm; a rapid rise from zero

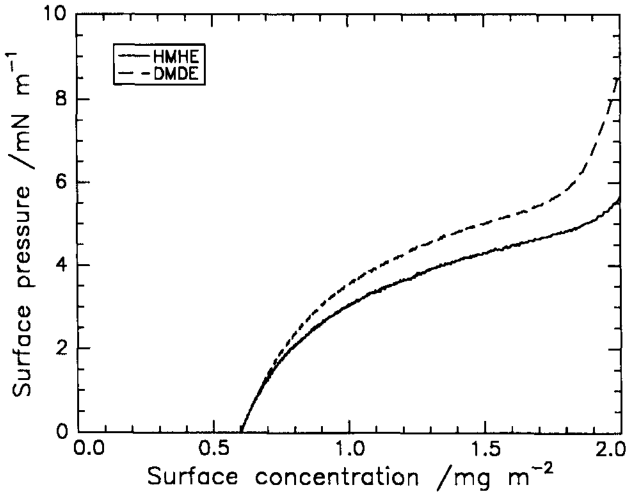

Figure 2 Surface pressure isotherm behaviour at 298 K for the fully hydrogenous and fully deuterated copolymers

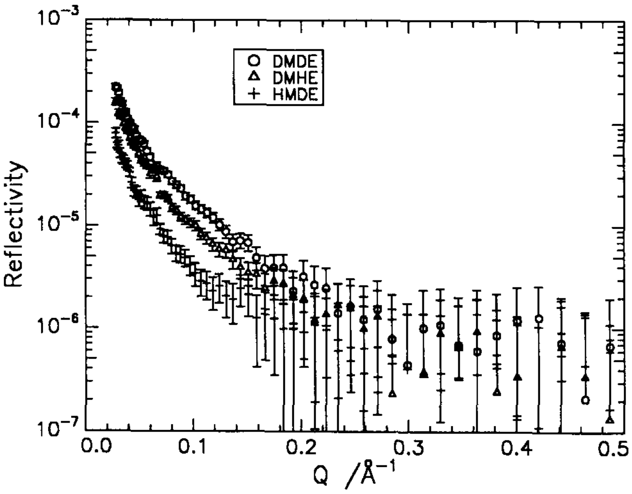

Figure 3 Background subtracted reflectometry profiles for partially and fully deuterated block copolymers spread on null reflecting water

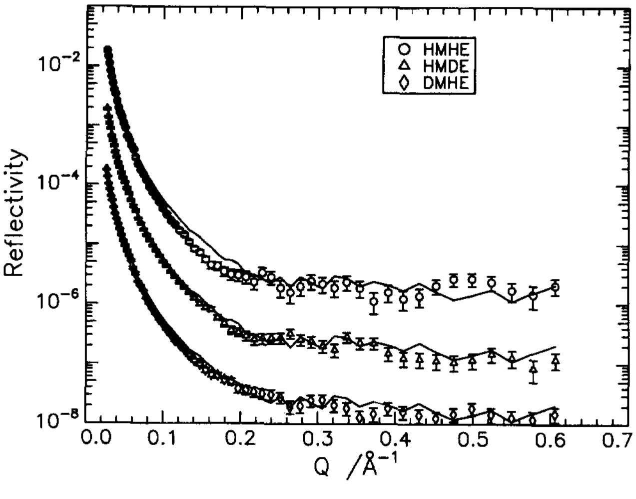

Figure 4 Reflectometry profiles for the part deuterated and fully hydrogenous block copolymers spread on D_2O. The solid line is the reflectivity of pure D_2O. The surface concentration of block copolymer in each case is 1.2 $mg\,m^{-2}$. Data sets have been artificially separated from each other by one decade in reflectivity for clarity

surface pressure at a finite surface concentration of copolymer. This is followed by a plateau region before a second rise in surface pressure begins at *ca* $2\,\mathrm{mg\,m^{-2}}$ of copolymer. Because obtaining partial structure factor requires six reflectivity profiles under different contrast conditions, only two surface concentrations of each block copolymer have been investigated by neutron reflectometry. These correspond to $0.6\,\mathrm{mg\,m^{-2}}$ and $1.2\,\mathrm{mg\,m^{-2}}$ of block copolymer, i.e. at the point where the surface pressure first becomes measurable and on the plateau region of the isotherm. *Figure 3* shows background subtracted reflectometry profiles for each of the deuterated isomers at the two surface concentrations when spread on NRW. The influence of an increasing content of deuterium in the block copolymer is clearly evident in the values of the reflectivity, as are the large errors for $Q > 0.25\,\text{Å}^{-1}$. *Figure 4* shows the reflectivity (without background subtraction) of the partially deuterated and fully hydrogenous copolymers spread on D_2O, within the errors of the reflectivity values only subtle differences can be distinguished from the reflectivity of pure D_2O which is shown as the solid line in *Figure 4*.

DISCUSSION

Although the neutron reflectometry profiles for each isomeric copolymer/subphase combination could be analysed using the exact optical matrix calculations as set out in our earlier paper[11], we proceed directly to the application of the kinematic approximation. This provides a more direct analysis of the data, additionally quantitative values for any separations between regions containing different species are relatively easily obtainable. The use of the optical matrix methods involves the modelling of the near surface region by a series of lamella parallel to the surface whose variation in composition normal to the surface mimics that of the spread copolymer. The centre-to-centre separation between the different regions in the surface layer does not appear as a distinct parameter from such fitting but has to be deduced from the values obtained. Furthermore, the multiplication of reflectivities by Q^4 implicit in the kinematic approximation analysis emphasizes the small differences between the reflectivity of clean D_2O and that supporting a spread film of block copolymer.

Notwithstanding the directness of the kinematic approximation, models are still required to interpret the partial structure factors in physical terms. To obtain the partial structure factors at each surface concentration, six equations of the type shown in equation (1) were set up using the reflectometry data from the different combinations of labelled polymer and subphase and solved for each value of Q, providing partial structure factors as a function of Q. The combinations of copolymer and subphase used were, DMDE/NRW, DMHE/NRW, HMDE/NRW HMHE/D_2O, DMHE/D_2O and HMDE/D_2O and the scattering length values used in equation (1) pertained to the total number of monomer units in each component block of the copolymer, i.e. they are composition weighted scattering lengths.

In our earlier paper[11] we showed, by using approximations to the self partial structure factors of differently labelled block copolymers, that the area per molecule obtained was identical and we concluded that there were no isotopic effects on the configuration of the polymer at the air–water interface. The self and cross partial structure factors obtained at the two surface concentrations of the block copolymers are shown in *Figures 5a* to *5f*. Dealing with the self partial structure factors first, it is evident that the increase in concentration has a significant effect on the methyl methacrylate block organization at the air–water interface, apart from indicating a higher concentration (as expected), the form of the curve also suggests the layer is thicker. These aspects will be quantified below. For the ethylene oxide block (*Figure 5b*), at the higher surface concentration the slightly steeper initial increase suggests a marginally thicker layer than that obtained at the lower surface concentration, but the differences in the actual concentration of ethylene oxide segments (proportional to the amplitude of the partial structure factor) do not appear to be significant. There appears to be no difference in the near surface water layer organization (*Figure 5c*) for the two surface concentrations explored.

Figure 5d shows a great difference in the separation between the methyl methacrylate layer and the near surface water layer for the two surface concentrations. Likewise there is some difference in the separation between the two components of the block copolymer and although this appears to be small in *Figure 5e*, we shall show that this corresponds to a quite marked separation. Finally, the data for the cross partial structure factor between ethylene oxide and water (*Figure 5f*) suggests a small separation between the two with little change as the surface concentration of block copolymer increases.

Self partial structure factors have been least squares fitted by a Gaussian distribution model;

$$h_{ii}(Q) = n_{ii}^2 \frac{\pi\sigma^2}{4} \exp\left(-Q^2\sigma^2/8\right) \tag{2}$$

Where n_{ii} is the number density of species i which is Gaussian distributed such that σ is the full width of the distribution at n_{ii}/e. Good fits between data and this model are obtained (*Figure 6*) but we should point out that equally good fits are obtained if a uniform layer model, described by equation (3), is used because the data does not extend sufficiently far in Q due to the background signal overwhelming the specular reflectivity

$$h_{ii}(Q) = \frac{1}{Q^2} n_{ii}^2 \sin^2(Qd/2) \tag{3}$$

We have used equation (2) in preference to equation (1) because it is intrinsically more physically relevant to polymer molecules. The number density used in fitting equation (2) to the data is that of the complete block in the copolymer. In equation (3), d is the thickness over which the number density n_{ii} is uniform. The self partial structure factor for the aqueous subphase has been fitted (*Figure 6c*) using a tanh distribution of water molecules, i.e.

$$n_s = n_{so}(0.5 + 0.5\tanh(z/\zeta)) \tag{4}$$

Where n_{so} is the bulk number density of water and ζ is the width parameter of the distribution normal to the surface with the depth indicated by z. The self partial structure factor obtained is;

$$h_{ss}(Q) = \frac{n_{so}^2\zeta^2\pi^2}{2} \operatorname{cosec h}^2\left(\zeta \frac{\pi}{2} Q\right) \tag{5}$$

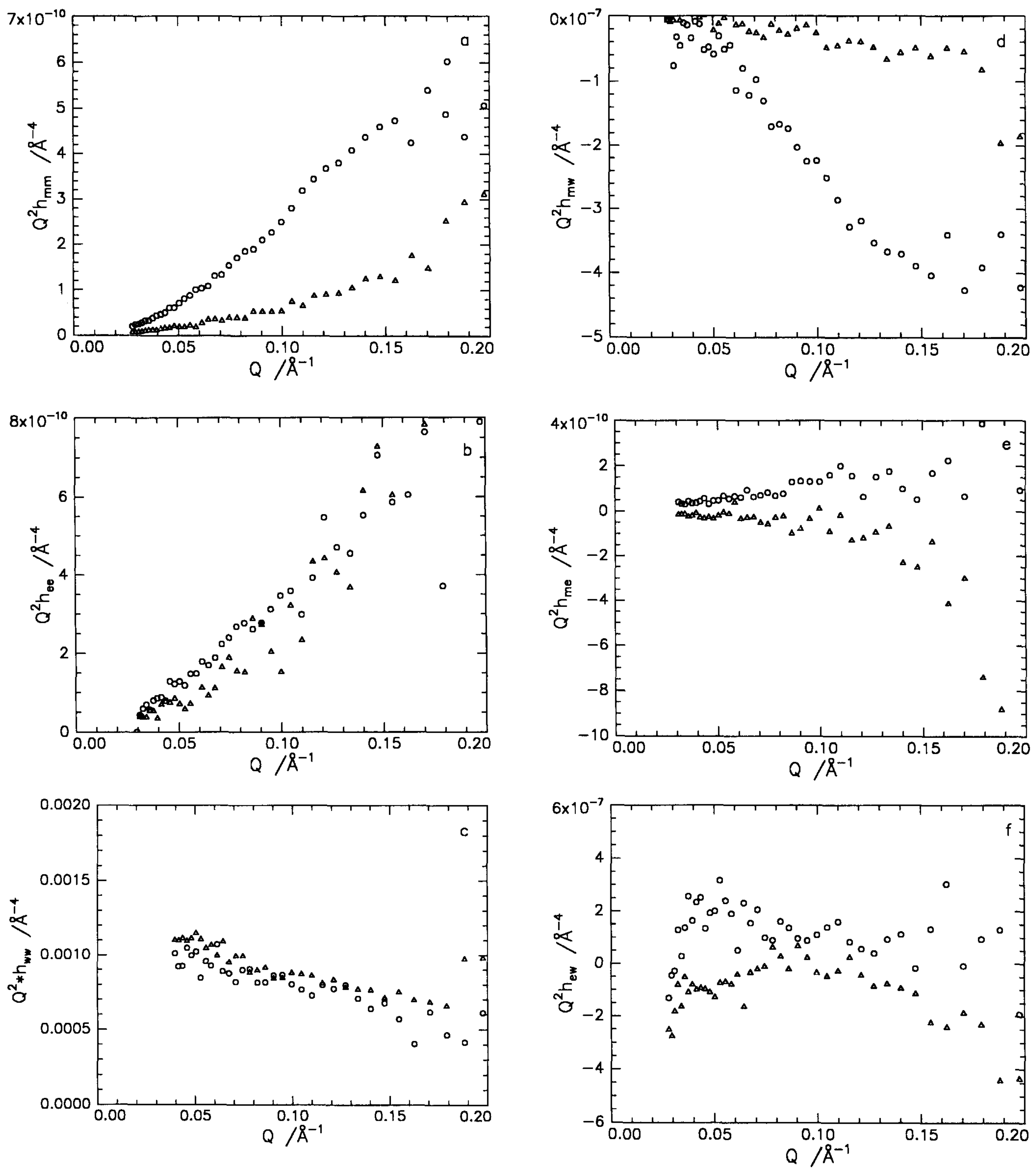

Figure 5 (a) Self partial structure factor for methyl methacrylate block of copolymer. (b) Self partial structure factor for ethylene oxide block of copolymer. (c) Self partial structure factor for the near surface layer of the subphase. (d) Cross partial structure factor between methyl methacrylate block and subphase. (e) Cross partial structure factor between methyl methacrylate and ethylene oxide blocks. (f) Cross partial structure factor between subphase and ethylene oxide block. In all cases ○ = 1.2 mg m^{-2}; △ = 0.6 mg m^{-2}

Table 2 gives the values of the various parameters obtained by fitting to the derived self partial structure factors. (W represents water).

The cross partial structure factors are given by products of the appropriate self partial structure factors multiplied by a geometric term depending on the approximate nature of the two distributions[16]. Hence for the cross partial structure factor between one block of the copolymer and the near surface water layer

$$h_{is}(Q) = \pm(h_{ii}(Q)h_{ss}(Q)^{1/2}\sin(Q\delta_{is})) \qquad (6)$$

Where δ_{is} is the separation of the centres of the two distributions. For the cross partial structure factor between the two blocks, i and j

$$h_{ij}(Q) = \pm(h_{ii}(Q)h_{jj}(Q))^{1/2}\cos(Q\delta_{ij}) \qquad (7)$$

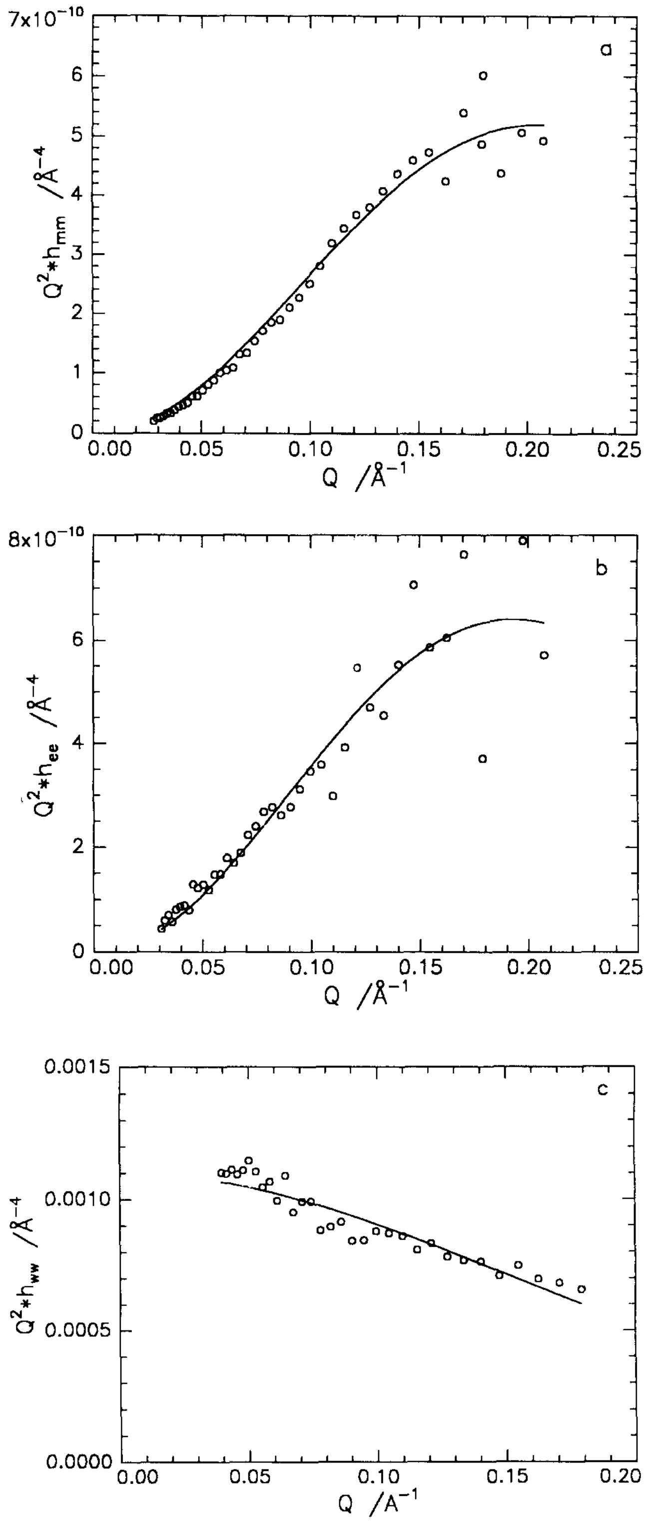

Figure 6 Fit of Gaussian distribution model (equation (2)) to the partial structure factor data for (a) methyl methacrylate and (b) ethylene oxide blocks at copolymer surface concentration of 1.2 mg m^{-2}. (c) Tanh distribution fitted to aqueous subphase partial structure factor

For the purposes of fitting, the self partial structure factors in equations (6) and (7) were generated from the theoretical equations (2 and 5) and the parameters given in *Table 2* fits to the data were made using only the separations as adjustable parameters. The calculated cross terms between subphase and polymer are sensitive to the values of δ_{is} as is shown in *Figure 7* where calculated cross partial structure factors are shown together with the least squares fit and the values obtained by this process are given in *Table 2*. We note that the fit to the cross partial structure factor between subphase and polyethylene oxide block is not good, particularly at low Q values. This may be due to the Q range approaching a region where the kinematic approximation is becoming invalid.

Table 2 Parameters of component distributions normal to the air/water interface

Γ_s	0.6 mg m^{-2}			1.2 mg m^{-2}		
Component	M	E	W	M	E	W
n_{ii} (10^{-5} Å^{-3})	1.2	2.2		1.51	1.87	
σ (Å)	8	9		14	12	
ζ (Å)			5			6
δ_{mc} (Å)	2			10		
δ_{mw} (Å)	1			6		
δ_{ew} (Å)	1			1		

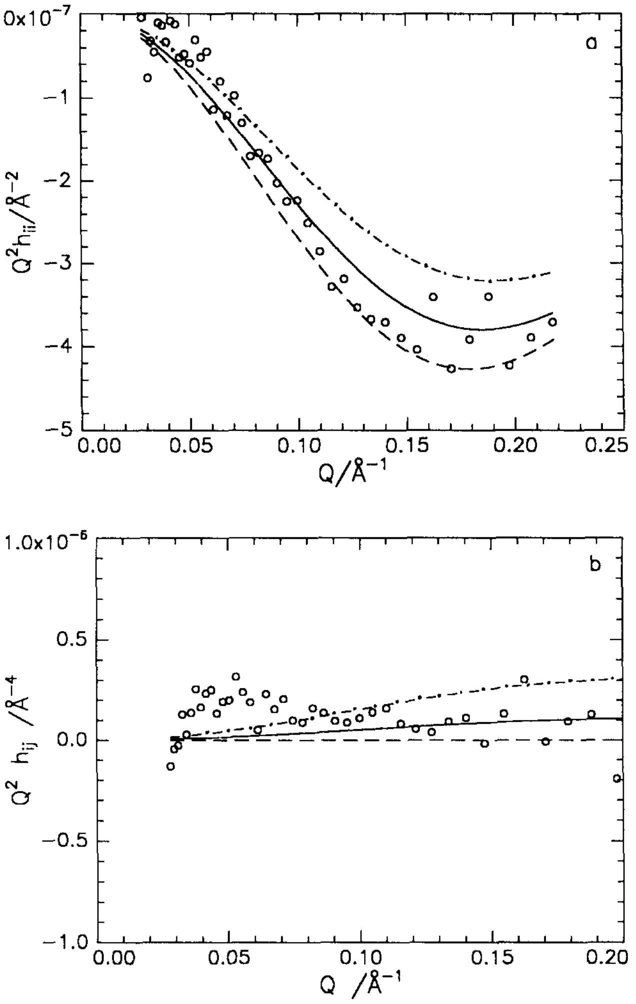

Figure 7 Cross partial structure factors at a copolymer surface concentration of 1.2 mg m^{-2} between subphase and: (a) methyl methacrylate block; (b) ethylene oxide block. The solid line is the least squares fits; dashed line, least squares value plus 1 Å; dashed-dot line, least squares value minus 1 Å

These values of n_{ii} and σ can be compared to the quantity of polymer actually spread on the water surface. For a Gaussian distribution the calculated surface

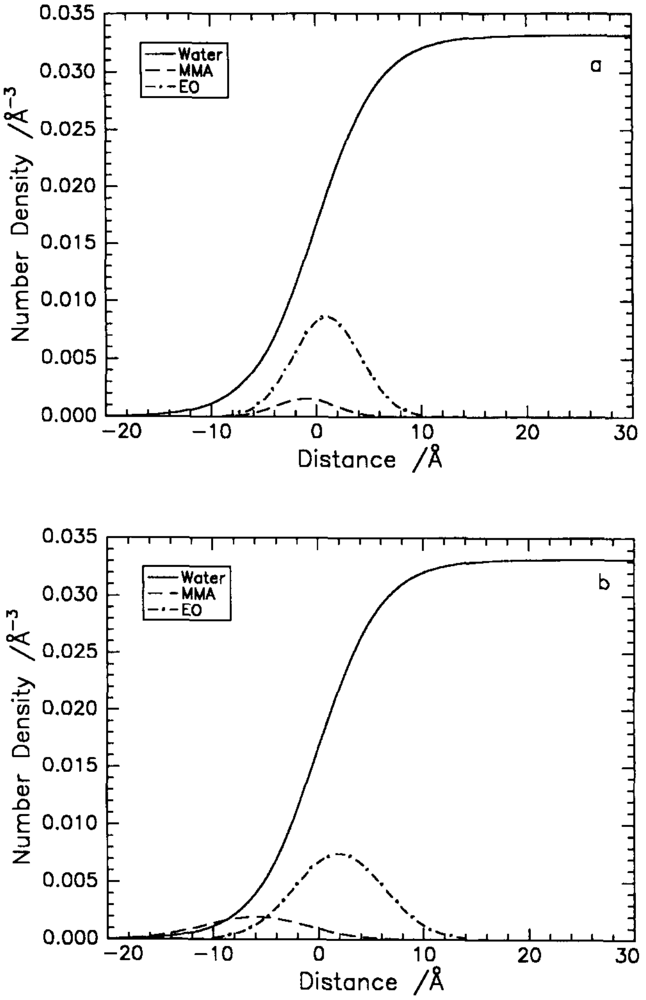

Figure 8 Spatial distributions of the components in the surface layer for the block copolymer film spread on water: (a) 0.6 mg m^{-2}; (b) 1.2 mg m^{-2}

concentration is given by

$$\Gamma_c = 10^{23}\,\frac{\sigma n_{ii}\pi^{1/2}}{2}\,M N_A^{-1}\ \mathrm{mg\,m^{-2}}$$

For the low surface concentration of 0.6 mg m^{-2}, the copolymer surface concentration obtained using the number densities and σ values derived from fitting to the partial structure factors is 0.62 mg m^{-2}, which is in very encouraging agreement with the amount spread. However for the highest surface concentration the calculated surface concentration is *ca* 1.1 mg m^{-2}, considerably below the amount spread on the surface. This disparity can be rationalized, albeit qualitatively, when the distributions of the segments in each of the copolymer blocks implied by the parameters in *Table 2* are plotted out, as in *Figure 8*. For the construction of this diagram, the segment density values of the methacrylate and ethylene oxide blocks in *Table 2* were multiplied by the number of monomer units per block averaged over all the copolymers used. At the lowest surface concentration investigated here, the two block components are mixed together and distributed over the same region and are wholly immersed in the aqueous subphase over a limited spatial region. At the higher concentration, there is a partial separation of the two blocks into two distinct spatial regions. The polyethylene oxide block stretches somewhat deeper into the subphase (although not by a great amount), whereas the methyl methacrylate block seems to be migrating more to the air-phase. At this higher concentration, the surface organization becomes identical to that reported by us earlier. We note that the ethylene oxide block has become distributed over a wider spatial region and that this block may actually extend deeper into the subphase, but becomes so highly diluted that the contribution of these deeper regions to the reflectometry profile is so small as to be unobservable.

Bijsterbosch *et al.*[17] have recently reported the application of neutron reflectometry data to block copolymers of polystyrene and polyethylene oxide spread at the air–water interface, and claimed that the system forms a brush like layer of polyethylene oxide at the air–water surface. Brush layer thicknesses of circa 500 Å are claimed for the modest polyethylene oxide block molecular weights used. These data were obtained using only hydrogenous polymer spread on D_2O and using the parabolic decay function from self consistent field theory to fit the data. Furthermore the range of Q used in the neutron reflectometry was very small, being from 0.01 Å^{-1} to 0.05 Å^{-1}. Nonetheless, the difference in the reflectivities of clean D_2O and in the presence of a spread polymer was marked. We observe no such difference here, the reflectivity of all copolymers spread on D_2O being dominated by that of D_2O (see *Figure 4*). As we have shown in earlier work[11], and also here, the difference between the reflectometry of clean D_2O and D_2O spread with hydrogenous polymer is almost negligible and there is no possibility to test for uniqueness of the model used. The difference due to the presence of copolymer is very subtle and one has to question whether the use of one model on one set of neutron contrast conditions is sufficient to provide a definitive description. In some earlier work we concluded that block copolymers of styrene and ethylene oxide form aggregates when spread at the air–water interface and consequently the local grafting density may vary widely, moreover the polystyrene ‘layer’ at the surface can be quite thick[18]. For the molecular weights of our copolymers, the grafting density range we have explored is *ca* 0.2–0.4 nm^{-2}. For this grafting density Bijsterbosch *et al.* recorded brush thicknesses of between 100 Å and 300 Å depending on the molecular weight of the polyethylene oxide block. As *Figure 8* shows, no such dimensions are tenable for the polymethyl methacrylate–polyethylene oxide diblock used by us. Moreover such dimensions have not been observed in surface excess layers in polyethylene oxide solutions nor in a methyl methacrylate copolymer with polyethylene oxide grafts. In this latter copolymer the grafting density is larger due to the number of grafts per molecule being larger than 1 (a linear diblock copolymer), however the thickness of the polyethylene oxide layer is only circa 30 Å. An important aspect in comparing these two approaches is the Q ranges used. Bijsterbosch *et al.* used a Q range from 0.01 to 0.05 Å^{-1}, the reflectivities in this region approach 1 and are unsuitable for application of the kinematic approximation. Our range of Q is from 0.02 Å^{-1} to 0.65 Å^{-1} (effectively 0.02 Å^{-1} to 0.25 Å^{-1} after background subtraction) and consequently contains more information on the shallower depths in the subphase. We have applied the identical parabolic form as for the scattering length density profile

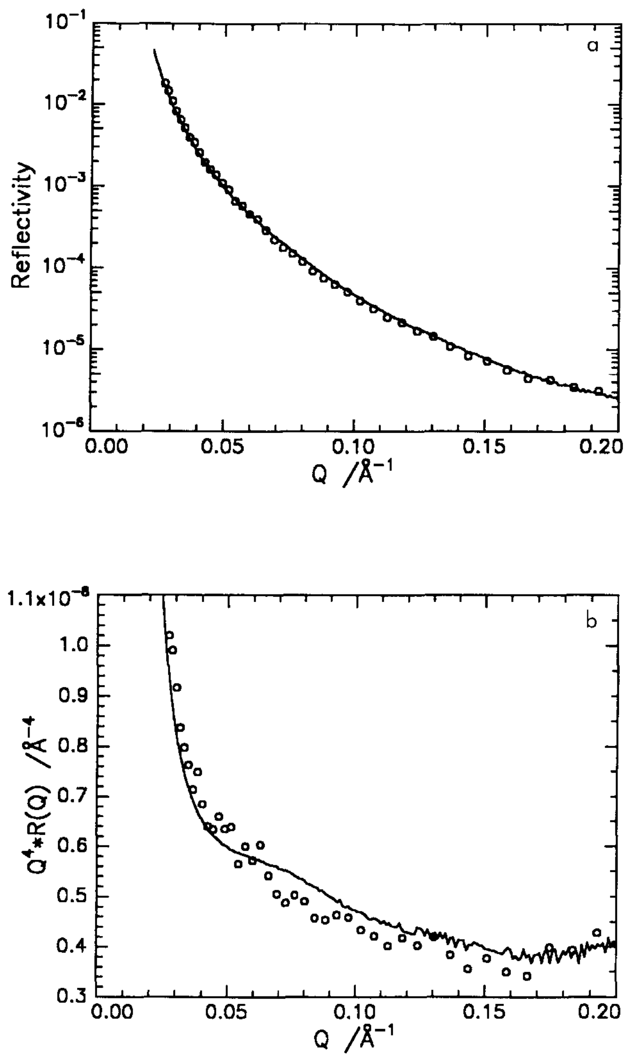

Figure 9 Fit of parabolic profile obtained from brush theory to reflectometry data of hydrogenous copolymer spread on D_2O. (a) Semi logarithmic plots for a surface concentration of 1.2 mg m^{-2}, solid line is fit of the parabolic model. (b) $Q^4R(Q)$ plots of the same data and fits as shown in (a)

to our data, and the outcome is shown in *Figure 9*. The data for the fully hydrogenous copolymer spread on D_2O were non-linearly least squares fitted by the parabolic function used by Bijsterbosch *et al.*, semi-logarithmic plots (*Figure 9a*) appear to be excellent. However, when the data and fit are replotted as $Q^4R(Q)$ as a function of Q (which is a much more sensitive way to establish differences between model and data), the discrepancies are clearly evident. Such $Q^4R(Q)$ plots are equivalent (apart from a scaling factor) to the self partial structure factor plots given in *Figure 5*. Evidently, the reflectivity is being dominated by that of the D_2O and the parameters of the parabolic profile respond more to factors associated with the D_2O subphase than the polymer. We also attempted to fit the parabolic form to the HMDE copolymer spread on NRW where only the DE component contributes to the reflectivity. No viable fits were obtained no matter what starting points were used in launching the fitting process. We are led to conclude that for the block copolymers we have used, the parabolic profile is inapplicable. Additionally there are other factors which lead one to expect that polyethylene oxide blocks would not stretch to form a brush like layer unless the surface graft density were very high. In homopolyethylene oxide solutions it is well known that a surface excess layer forms due to the lower surface energy of the polyethylene oxide. To reduce the surface tension of the air–water interface below that of polyethylene oxide requires *very* high surface concentrations of block copolymer, so much so that film collapse sets in before the necessary concentrations are reached. For the two concentrations used here there is no thermodynamic driving force to promote the formation of a brush-like layer of polyethylene oxide.

CONCLUSIONS

Using neutron reflectometry on selectivity deuterium labelled linear diblock copolymers of methyl methacrylate and ethylene oxide it has been shown that a 'surface phase separation' takes place at some critical surface concentration. This conclusion has been made based on application of the kinematic approximation to the neutron reflectometry data and the evaluation of partial structure factors. In addition to providing quantitative parameters for the composition and thickness of the regions containing methyl methacrylate and ethylene oxide, it also provided the separations between each of these regions, as well as the surface region where the water differed in number density from the bulk. The 'surface phase separation' observed rationalizes the variation in relaxation times noted for spread films when perturbed by capillary waves.

There was no basis for applying the brush type profile analysis to either hydrogenous polymer spread on D_2O or partially deuterated polymer spread on null reflecting water. Although the theoretical model may apply to some situations, it seems that for polymers at the air–water interface its applications may be sparse.

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