

Influence of Dissolved Polymer on the Dimensions of a Tethered Polymer Layer for a Graft Copolymer Spread at the Air–Aqueous Solution Interface

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A graft copolymer with a polynorbornene backbone and deuteriopoly(ethylene oxide) grafts has been spread on aqueous subphases with dissolved hydrogenous poly(ethylene oxide) at different concentrations. The surface pressure isotherms of the spread film are very different from that obtained on water alone. A negative surface pressure is initially observed and a zero surface pressure is obtained only at a higher surface concentration of the spread graft copolymer, indicating the expulsion of dissolved poly(ethylene oxide) from the near surface. At a higher surface concentration of the graft copolymer, there is a “phase transition” in the isotherm, the surface concentration at which this is obtained depending on the concentration of poly(ethylene oxide) in the aqueous subphase. Neutron reflectometry has been applied to determine the distribution of the deuterated ethylene oxide segments as a function of the surface concentration and poly(ethylene oxide) concentration in the sub phase. The graft layer consists of a uniform composition region with a parabolic “tail”. The thickness of the uniform region is smaller than that obtained in the absence of dissolved polymer and at the highest poly(ethylene oxide) concentration in the subphase the dimensions of this layer are reduced relative to those for the lower concentrations of poly(ethylene oxide). The extent of the parabolic decay region is not significantly influenced by the dissolved polymer but the maximum thickness of this region is reached at a lower surface concentration compared to that for the graft copolymer spread on water. The dissolved polymer appears not to provide screening in this parabolic region but instead is a source of additional excluded volume interactions that cause the extension of the poly(ethylene oxide) grafts.

Introduction

The spatial organization and composition distribution in the layer formed when polymer molecules are attached by one end (‘tethered’) to an interface have been a focus for considerable attention both theoretically^{1–26} and experimentally for a number of years. Various aspects of such tethered layers have been examined when they are immersed either in a polymer melt or in a low molecular weight solvent. The aspect of interest is generally the extent to which the tethered polymer layer conforms to the description as being “brush-like”, wherein there is considerable stretching of the molecules when the distance between the tethering points is smaller than the radius of gyration of the tethered molecules. Much of the early experimental investigation of such layers used the surface forces apparatus to infer the segment density distribution of two tethered polymer layers from their force distance profiles.^{27–30} The application of ion beam analysis^{7,31–33} and neutron reflectometry^{12,13,30,34–36} to polymer systems not only extended such investigation to bulk polymer melts but also gave direct estimates of the tethered layer thickness and hence provided evidence for tethered molecule stretching as their concentration at the surface or interface increased. Small-angle neutron scattering has also been used to investigate the dimensions of tethered layers.³⁷

Such end-attached polymer molecules have a considerable number of practical applications and play important roles in other aspects of polymer interfacial behavior. They are extremely

pertinent to the stabilization of block copolymer micelles,³⁸ dispersions, inhibition of protein absorption,³⁹ control of dynamic fluctuations at fluid interfaces,^{40–44} and interfacial toughening between immiscible polymers, and brush-like layers can modify severely the kinetics of reaction at the interface between immiscible polymers.^{45–47}

In dilute solution under good solvent conditions, polymer molecules expand because of the excluded volume effect. Above the overlap concentration, c^* , screening effects become manifest and attenuate the intramolecular excluded volume effects⁴⁸ and the polymer molecule dimensions decrease to their equilibrium unperturbed values. This latter state is reached at concentrations considerably less than that corresponding to bulk polymer, i.e., there is a finite volume fraction of solvent in the solution.⁴⁹ The excluded volume effect is also responsible for stretching tethered molecules when the interfacial grafting density is sufficiently large.⁶ Consequently, incorporating a polymer chemically identical to the tethered polymer into the surrounding solvent should also produce a reduction in the brush layer dimensions.

The original theories of grafted brush-like polymer layers envisioned the molecules having stationary tethering points on a solid surface.³ From an experimental point of view it has often been found impossible to reach a sufficiently high degree of grafting of polymer molecules on solid surfaces such that “dry brush layer”^{9,50} behavior is approached when bulk polymer melts surround the tethered chains and the range of grafting densities

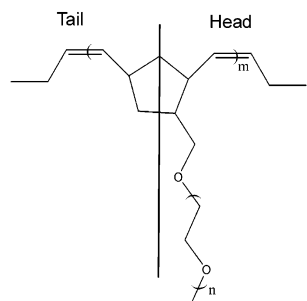


Figure 1. Schematic formula of graft copolymer.

accessible is rather restricted. Attempts to overcome this limitation have used spread films of copolymers on a liquid subphase, the subphase being a solvent for one of the copolymer components. Kent et al.^{12,13,34,51} investigated a polydimethyl siloxane–polystyrene diblock copolymer spread on ethyl benzoate, and we have used a graft copolymer with poly(ethylene oxide) (PEO) grafts spread on the surface of water.^{52,53} For the latter case, although the PEO grafts were of only modest molecular weight, they were stretched up to three times their radius of gyration on immersion in the aqueous subphase. Furthermore, the nature of the grafted, immersed layer of PEO changed as the depth into the subphase increased. Near the air–water interface, the PEO layer was best described as a layer of uniform segment density; at greater depths, the distribution became parabolic in nature. The thickness of the uniform layer region showed a dependence on surface concentration that was in qualitative agreement with the predictions of Szleifer²⁶ concerning unfavorable interactions between components of a copolymer spread at the air–liquid interface. We discuss here the influence of the concentration of free poly(ethylene oxide) dissolved in the subphase on the dimensions and composition distribution of the graft layer and contrast the behavior with that reported for the spread diblock copolymer of polydimethyl siloxane–polystyrene referred to earlier.

Experimental Section

Copolymer and Subphase Homopolymer. A single graft copolymer with a polynorbornene backbone and deuteriopoly(ethylene oxide) grafts was employed. The synthesis of this copolymer by a combination of anionic and ring-opening metathesis polymerizations has been detailed in earlier publications,^{52,53} and a schematic structure of the graft copolymer is shown in Figure 1. For the copolymer discussed here, the degree of polymerization of the backbone (m in Figure 1) was 50 and that of the deuterated poly(ethylene oxide) (n) was 25. The total molecular weight of the polymer was $79\,500\text{ g mol}^{-1}$.

Hydrogenous poly(ethylene oxide) dissolved in the aqueous subphase was obtained from Polysciences and has a quoted molecular weight of $105\,000\text{ g mol}^{-1}$.

Surface Tension and Surface Pressure Isotherms. The surface tension of each aqueous poly(ethylene oxide) solution was determined by the Wilhelmy plate method, 10 individual measurements being made for each solution and the results averaged.

Surface pressure isotherms at 298 K for the spread copolymer film on each aqueous PEO subphase were obtained using a NIMA model 2001 Langmuir trough (NIMA Technology, Coventry, U.K.). The trough was filled with the aqueous PEO solution, the surface of which was repeatedly aspirated and swept by the trough barriers. The solution was then allowed to equilibrate for 15 min to ensure that the equilibrium surface excess concentration was obtained. During this time, the surface

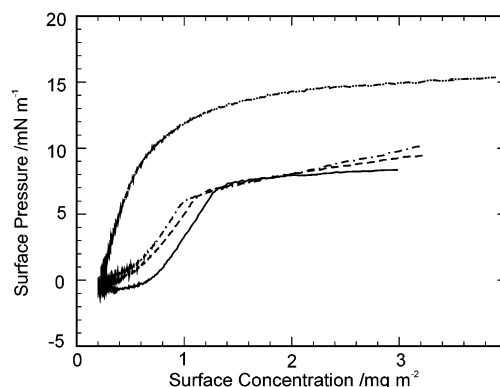


Figure 2. Surface pressure isotherms for the graft copolymer spread on aqueous solutions of poly(ethylene oxide). (—) 0.1% PEO subphase; (---) 2% PEO subphase; (- - -) 5% PEO subphase; (- · - ·) water subphase.

tension was monitored, a constant value being obtained in ca. one minute into the equilibration time. Monitoring the surface tension for up to 2 h also showed no change, thus there was no evidence of a slow approach to equilibrium.⁵⁴

The copolymer film was then spread on the solution by dispensing a few microliters of a chloroform solution of the copolymer with an accurately known concentration of ca. 1.0 mg mL^{-1} . The spread film was then left for 15 min to ensure complete evaporation of the chloroform before compressing the film at a rate of $30\text{ cm}^2\text{ min}^{-1}$. The useable area of the trough was ca. 900 cm^2 and isotherm data needed 30 min for collection.

Neutron Reflectometry. Neutron reflectometry data were collected using the SURF reflectometer on the pulsed neutron source, ISIS, at the Rutherford Appleton Laboratory, Didcot, U.K. The aqueous subphase was prepared by dissolving hydrogenous poly(ethylene oxide) in null reflecting water, the latter being a mixture of light and heavy water that has a net neutron scattering length density of zero, the volume fraction of light water being 0.92. The poly(ethylene oxide) solutions were placed in a NIMA rectangular Langmuir trough, and a solution of the graft copolymer in chloroform was dispensed on to the surface from a microsyringe. To prevent excessive $\text{H}_2\text{O}/\text{D}_2\text{O}$ exchange with the atmosphere, the trough was enclosed in a box with quartz inlet and outlet windows for the incident and specularly reflected neutron beam. The concentrations of poly(ethylene oxide) in the subphase that were used were 0.1% w/v, 2% w/v, and 5% w/v, for higher concentrations the solutions became very viscous and cleaning of the troughs to ensure complete removal of poly(ethylene oxide) was both difficult and tedious. The range of surface concentrations of the spread graft copolymer film explored was from 0.3 mg m^{-2} to 4.0 mg m^{-2} . The scattering vector (Q) range normal to the surface that was explored was $0.02 \leq Q/\text{\AA}^{-1} \leq 0.6$, and absolute values for the reflectivity were obtained using a calibration factor calculated using the reflectivity from a clean D_2O surface.

Results

Surface Tension and Surface Pressure Isotherms. For the 0.1%, 2.0%, and 5.0% w/v aqueous PEO solutions, the average surface tensions were 63.1 ± 0.6 , 60.6 ± 0.5 , and $53.8 \pm 0.6\text{ mN m}^{-1}$, respectively. Figure 2 shows the surface pressure isotherms obtained on each of the aqueous PEO isotherms and on a pure water subphase for comparison. There are evident differences between the isotherms on aqueous PEO compared to that on pure water. For the latter the surface pressure increases immediately on compression and there is a smooth decline in

TABLE 1: Surface Concentrations (mg m^{-2}) and Normalized Grafting Densities of Spread Graft Copolymer Films Where Surface Pressure Behavior Changes

PEO subphase concentration %w/v	$\pi =$ 0 mN m^{-1}	"phase transition" in π	σ^* for "phase transition"
0.1	0.65	1.38	3.7
2.0	0.36	1.18	3.16
5.0	0.22	1.05	2.81

the rate of increase in surface pressure with surface concentration until a small monotonic rate of increase prevails for surface concentrations greater than ca. 1.5 mg m^{-2} . The isotherms for the spread films on aqueous PEO subphases show an initial decrease in surface pressure from zero, then a slow increase with increasing surface concentration that accelerates to a region where the surface pressure increases at a constant rate with surface concentration. Finally, there is an abrupt break in the surface pressure isotherm ("phase transition") at a surface concentration that decreases with increasing concentration of PEO in the subphase. Table 1 gives the values of the surface concentration of spread copolymer where the surface pressure regains a value of zero and where the "phase transition" in the surface pressure isotherm takes place.

Neutron Reflectometry. Representative plots of neutron reflectometry data for the extremes of the subphase PEO concentration and for a wide range of the graft copolymer spread film surface concentration (Γ_s) are shown in Figure 3. At the lowest concentration of PEO in the subphase, the reflectometry data are similar to those observed for the graft copolymer spread on pure water, i.e., in the absence of homopolymer. For the highest surface concentration of the spread film (4.0 mg m^{-2}), the reflectivity is larger in magnitude than that for the equivalent spread copolymer film surface concentration on pure water. The reflectivity data for the lower surface concentration (0.7 mg m^{-2}) is clearly distinguishable from that for 4 mg m^{-2} and we note the two curves are not parallel to each other, suggesting that neither the surface layer thickness nor its deuterioethylene oxide content are similar to each other for these two surface concentrations. On increasing the subphase PEO concentration to 5% w/v, the data are markedly different from that for the lower PEO subphase concentrations. For the highest surface concentration of the graft copolymer spread film there appears to be little change in the nature of the reflectivity profile relative to that for the 0.1% w/v PEO subphase. However, for a spread copolymer film concentration of 0.7 mg m^{-2} , the reflectivity data is rather like that for $\Gamma_s = 4.0 \text{ mg m}^{-2}$. Compared to the reflectivity obtained on the 0.1% w/v PEO subphase, a larger reflectivity is observed and the decrease in reflectivity with Q is more rapid for the lowest surface concentration of the spread film. These observations suggest that both the layer thickness and its deuterioethylene oxide content have increased for the film surface concentration of 0.7 mg m^{-2} spread on an aqueous subphase with a PEO concentration of 5% w/v.

Scattering length densities of the various units in the graft copolymer and the subphase are given in Table 2. The scattering length density of a copolymer backbone segment is about an order of magnitude smaller than that of deuterioethylene oxide and effectively approximates to zero. For the combination of isotopic labeling used here, the contribution of the polynorbornene backbone to the reflectivity appears to be negligible. Simulations of the reflectivity using the exact optical matrix method confirm this assumption. For simulating the reflectivity we used a deuterio PEO layer thickness of 30 \AA with a dPEO

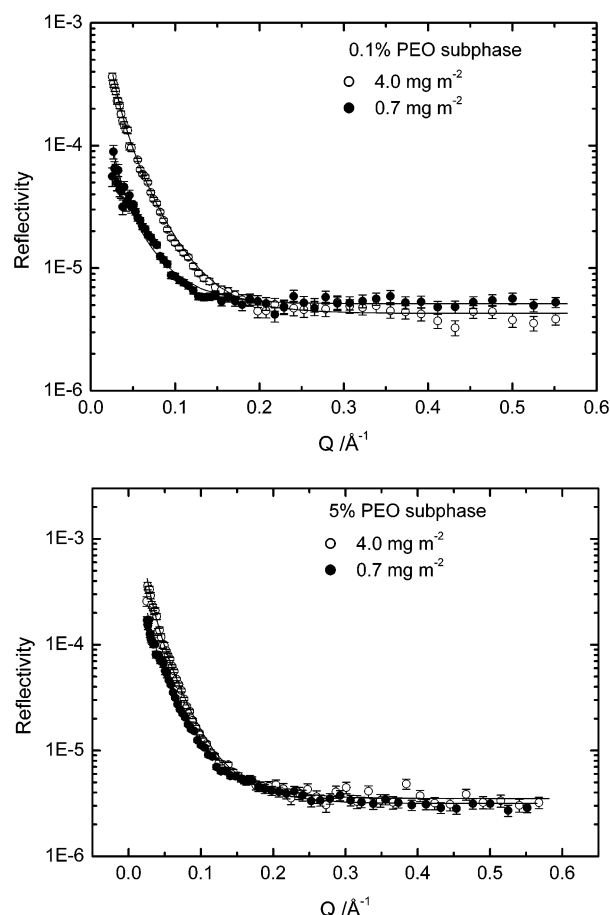


Figure 3. (a) Experimental reflectivity data for graft copolymer spread at surface concentrations of 0.7 mg m^{-2} (●) and 4.0 mg m^{-2} (○) on an aqueous subphase containing 0.1% w/v PEO. (b) Experimental reflectivity data for graft copolymer spread at surface concentrations of 0.7 mg m^{-2} (●) and 4.0 mg m^{-2} (○) on an aqueous subphase containing 5.0% w/v PEO.

TABLE 2: Scattering Length Densities

unit	$\Sigma b/10^{-4} \text{ \AA}$	$\rho/10^{-6} \text{ \AA}^{-2}$
H ₂ O	-1.68	-0.56
D ₂ O	1.92	6.35
ethylene oxide	0.41	0.56
deuterated ethylene oxide	4.58	6.33
norbornene	1.78	0.89

volume fraction of 0.2 and root-mean-square roughness at the subphase of 10 \AA . This latter factor simulates the gradual decline in deuterio PEO content as the layer extends into the subphase. Figure 4 shows two calculated reflectivity profiles, one for a single layer of deuterio PEO as described above and the second for a two-layer system where a 5 \AA thick film containing only hydrogenous polynorbornene constitutes the upper layer with a roughness of 2.5 \AA to mimic capillary wave fluctuations, these being the characteristics of this layer as obtained in our earlier papers. In both cases, the subphase was null reflecting water and the two sets of reflectivity data are essentially identical. Consequently, in analyzing the reflectivity from the spread graft copolymer films, we have used the model for the graft PEO distribution used in our earlier papers^{53,55} and we have attributed all the reflectivity to the distribution of the deuterated graft poly(ethylene oxide). The model is shown schematically in Figure 5 and has a uniform composition upper layer with a parabolic "tail" extending into the subphase. In terms of the various parameters identified in Figure 5, the nonlinear least-squares

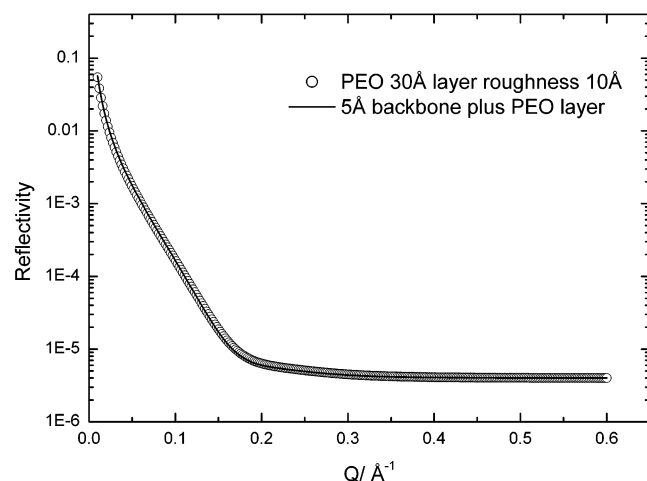


Figure 4. Simulated reflectivity for a DPEO layer of thickness 30 Å with a polymer volume fraction of 0.2 (○) compared to that for an identical DPEO layer with a 5 Å thick polynorbornene backbone layer (solid line).

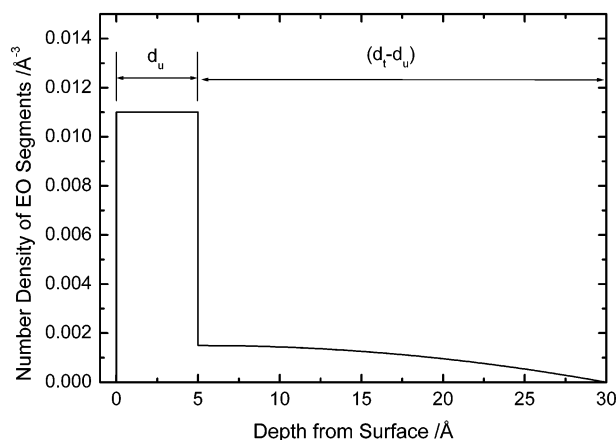


Figure 5. Schematic of the segment density distribution used to model the experimental reflectivity data.

fitting adjusted n_u and n_{i2} , the number density of deuterio ethylene oxide segments in the uniform layer and at the start of the parabolic decay region respectively, d_u and $(d_t - d_u)$ the thickness of the uniform layer and the decay distance of the parabolic decay region. Examples of typical fits to the data using this model are included as the solid lines in Figure 2.

Values of d_u and $(d_t - d_u)$ obtained from these fits are plotted as a function of normalized grafting density, σ^* , in Figures 6 and 7. The thickness of each layer is normalized by the radius of gyration (R_g) in water of PEO⁵⁶ of equivalent molecular weight as the grafts and the normalized grafting density is also calculated using this value of radius of gyration. In calculating σ^* , the grafting density, σ , is obtained assuming that all PEO grafts are immersed in the aqueous subphase and $\sigma^* = \sigma \pi R_g^2$. For the lowest subphase PEO concentration of 0.1% w/v, $(d_t - d_u)/R_g$ varies with σ^* in a manner that is essentially identical to that when the polymer is spread on pure water. The extent of the parabolic decay region increases with σ^* and exhibits a weak maximum for $6 \lesssim \sigma^* \lesssim 8$. The uniform layer thickness, d_u , has a very different behavior for the 0.1% PEO subphase. At low values of σ^* , d_u/R_g is the same magnitude for both pure water and 0.1% PEO-containing subphases. However, for the latter system, the increase in d_u/R_g with σ^* only reaches the modest value of 0.5 and remains at this value over much of the range of σ^* explored. In the absence of PEO in the subphase,

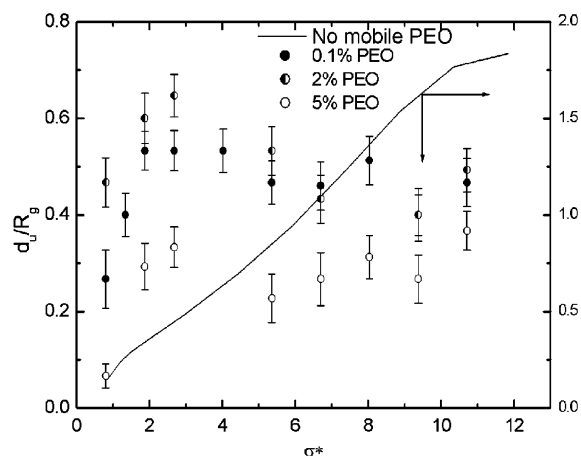


Figure 6. Dependence of the uniform layer thickness of the graft DPEO (normalized to the radius of gyration of the equivalent molecular weight PEO in free solution) on the normalized grafting density. Solid line shows values obtained in the absence of PEO in solution.⁵³

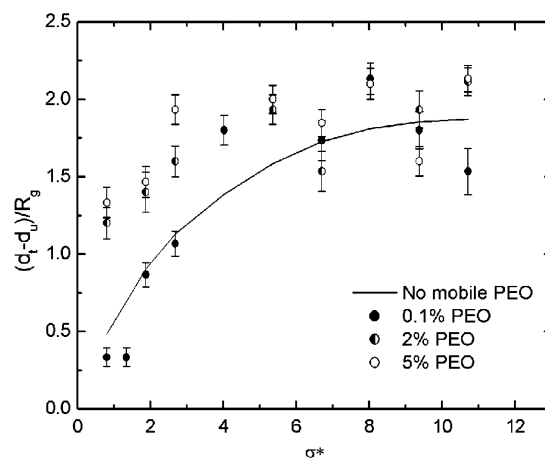


Figure 7. The parabolic region thickness (normalized by radius of gyration of PEO in solution) as a function of the normalized grafting density. Solid line shows values obtained in the absence of PEO in solution.⁵³

d_u/R_g increased to ca. 1.6 over this same range of σ^* . For a subphase PEO concentration of 2% w/v, the variation of d_u with σ^* is very similar to that for 0.1% w/v PEO in the subphase. At the highest PEO subphase concentration of 5% w/v, d_u/R_g is half the magnitude of that observed for the lower PEO subphase concentrations. The extents of the parabolic decay region are all essentially the same at ca. $2R_g$ for $\sigma^* = 6$ and above for all subphases used. The values of $(d_t - d_u)$ show an initial dependence on σ^* but attain a constant value at a value of σ^* that depends on the subphase PEO concentration. These σ^* values for the 0.1%, 2%, and 5% w/v PEO solutions are ca. 4, 3, and 2.5, respectively.

The σ^* dependence of the deuterio ethylene oxide segment number density in the uniform layer, n_u , is essentially identical for graft copolymer films spread on subphases with 0.1% and 2% w/v PEO increasing slowly to an asymptotic value of $\sim 9 \times 10^{-3} \text{\AA}^{-3}$ for $\sigma^* \approx 8$. For the 5% w/v PEO subphase, n_u is essentially constant at $\sim 1.2 \times 10^{-2} \text{\AA}^{-3}$ over the whole range of σ^* (Figure 8a). The number density of grafted PEO segments at the outset of the parabolic region, n_{i2} is constant at ca. $2 \times 10^{-3} \text{\AA}^{-3}$ for the copolymer spread on 2% and 5% w/v PEO solutions, whereas for the 0.1% w/v PEO solution a gradual increase is noted that eventually attains the same value of $2 \times 10^{-3} \text{\AA}^{-3}$ at the highest values of σ^* (Figure 8b).

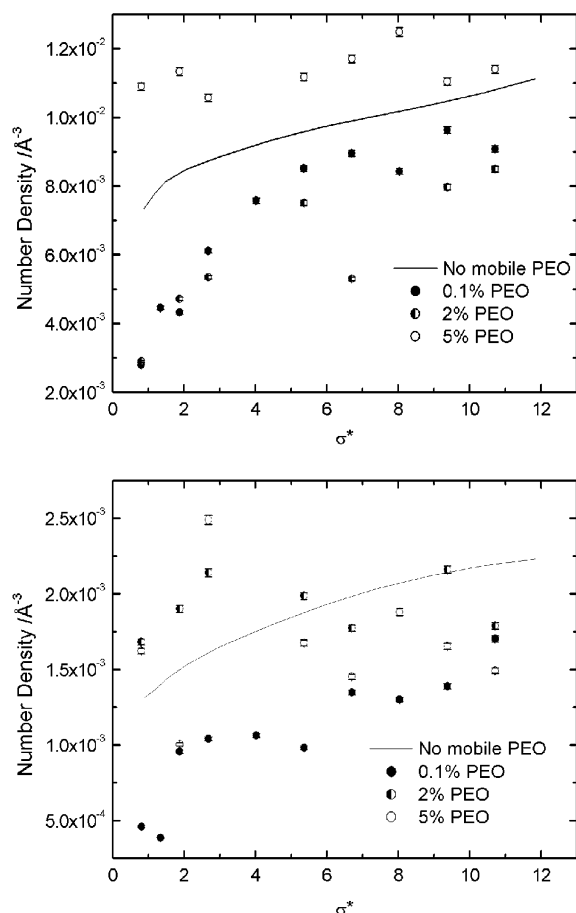


Figure 8. (a) Number density of grafted poly(ethylene oxide) segments in the uniform layer as a function of normalized surface grafting at each of PEO concentrations in the subphase. (b) Number density of grafted poly(ethylene oxide) segments at the start of the parabolic composition distribution region as a function of the normalized surface grafting and for each PEO containing subphase. Solid line shows values obtained in the absence of PEO in solution.⁵³

Discussion

The only data available that addresses the same topic of the influence of dissolved polymer on the dimensions of grafted layers is that of Lee et al.¹⁷ for spread films of a diblock poly-(dimethylsiloxane)–polystyrene copolymer on ethyl benzoate solutions of polystyrene. In common with that observed here, the dissolved polystyrene caused a reduction in the dimensions of the grafted polystyrene layer relative to those observed when spread on ethyl benzoate alone. As the surface concentration of the spread copolymer was increased, the grafted layer dimensions exhibited a linear increase with increasing σ^* . Although not quoted by Lee et al., it appears that the scaling exponent for the dependence of layer thickness on σ^* was ca. 0.4, i.e., a much stronger dependence than predicted by the scaling law theories. Earlier they found that the exponent obtained for the copolymer spread on ethyl benzoate alone was weaker than the scaling law prediction. No data was presented for the dependence of the composition of the grafted layer on σ^* and concentration of polystyrene in the mobile phase, although it appears that the volume fraction of grafted polystyrene in the surface layer was increased over that obtained in the absence of dissolved polystyrene.

The decrease in the surface tension of the aqueous PEO solutions relative to that of pure water has been examined for many years and is commensurate with the formation of a surface excess layer at the air–water interface.^{54,57} Cao and Kim⁵⁸

determined the molecular weight dependence of the surface tension of PEO for molecular weights ranging from 0.425×10^3 to $1000 \times 10^3 \text{ g mol}^{-1}$ and a bulk solution concentration range from $\sim 10^{-4}\%$ to 10% w/v. For concentrations less than $\sim 0.1\%$ w/v, all molecular weights showed identical variation of surface tension with concentration. At higher concentrations, a distinct molecular weight dependence of the surface tension is observed and the largest reduction in surface tension from that of water alone was noted for a PEO molecular weight of $85 \times 10^3 \text{ g mol}^{-1}$, i.e., very similar to the molecular weight of the PEO used here. For PEO molecular weights above and below $85 \times 10^3 \text{ g mol}^{-1}$, the reduction in surface tension on increasing the concentration of PEO in solution was much smaller. This behavior was attributed to the hydrophile–lipophile balance (HLB), determined by the end groups, and the increased solubility of PEO with increased molecular weight due to hydrogen bond formation with water. As the PEO molecules become more hydrophobic, their surface energy decreases, increasing the concentration in the surface excess region and reducing the surface tension. Competing with this is the increased solubility as the molecular weight increases and hence the surface tension reduction goes through a maximum at a particular molecular weight of PEO. To aid the interpretation of the grafted layer dimensions obtained here, the key factors from these data appear to be (1) the molecular weight of the PEO used is very close to that where the maximum reduction in surface tension is observed, i.e., the PEO concentration in the surface excess layer will be at its greatest; (2) the surface excess layer is hydrophobic and becomes increasingly so as the solution concentration increases.

A detailed neutron reflectometry study⁵⁷ of 0.1% w/v PEO (molecular weight $87 \times 10^3 \text{ g mol}^{-1}$) solutions has been reported, the excess layer having a thickness of ca. 20 \AA and a number density of ethylene oxide segments of $3.4 \times 10^{-3} \text{ \AA}^{-3}$. The considerable fall in surface tension for the 5% w/v PEO solution suggests that the number density of poly(ethylene oxide) in the surface layer is considerably larger than that for the 0.1% and 2% w/v solutions. This conclusion is also supported by the surface pressure isotherms of the spread copolymer film (Figure 2). For both the 0.1% and 2% w/v PEO solutions, the surface pressure is initially negative on spreading the copolymer, i.e., material has been desorbed from the interfacial region. The dissolved PEO in the surface excess region is displaced by the PEO grafts of the copolymer to deeper within the subphase. For the 0.1% w/v PEO solution, the surface concentration of spread copolymer film at zero surface pressure obtained corresponds to the grafted PEO having a number density of $3.6 \times 10^{-3} \text{ \AA}^{-3}$, i.e., exactly the concentration in the surface excess layer of a 0.1% w/v PEO solution. Hence, the poly(ethylene oxide) grafts have completely expelled the mobile polymer from the surface excess region. For the higher concentration PEO subphases, zero surface pressure is recovered at lower spread film concentrations and suggests that some of mobile PEO is retained in the surface excess region. Consequently, although the surface tensions of the 0.1% and 2% w/v solutions are reasonably close, we cannot presume these two solutions to have the same surface excess layer structure. The position of the phase transition in the isotherms at high surface concentration is also correlated to the subphase concentration, the transition to a film with a higher resistance to compression is rather similar to that observed for low molecular weight spread molecules entering the intermediate region from the liquid-expanded isotherm region. Evidently, the presence of mobile polymer is the cause of the abruptness of the transition compared

to that observed for spread films on water alone, but the nature of the direct cause of the abrupt transition is not evident.

The influence of dissolved ("mobile") polymer on the dimensions of a layer of grafted polymer molecules has been described using scaling laws³ and self-consistent field theory.⁵⁹ In these discussions, the grafted polymer is presumed to be of high molecular weight and this molecular weight is greater than that of the mobile chains. Under these conditions, scaling theory divides the effects of the mobile polymer into two broad classes. For low concentrations of mobile polymer, and assuming that the grafting density is sufficient to promote strong stretching of the grafted molecules, the grafted molecules remain strongly stretched. When the concentration of mobile chains exceeds a critical concentration ($\propto \sigma^{*2/3}$) and becomes semidilute, a change from strong stretching to weak stretching is predicted, this change becoming progressive as the mobile concentration increases above the critical concentration noted above. For this second class of behavior there are two subdivisions depending on whether the mobile polymer or the grafted chains are dominant, i.e., whether the volume fraction of mobile polymer is greater or smaller than that of the grafted polymer in the grafted layer. Where mobile chain dominance is anticipated, the grafted layer thickness, h , should scale with σ^* in exactly the same way in the absence of mobile polymer, i.e.

$$h \propto \sigma^{*1/3}$$

When the grafted chains dominate in the tethered layer a very different scaling law is predicted,

$$h \propto \sigma^*$$

As noted earlier, mobile PEO excess layer thickness is approximately 20 Å and the ethylene oxide segment number density in this layer is $3.4 \times 10^{-3} \text{ Å}^{-3}$, significantly less than the number density of graft ethylene oxide segments in the uniform layer region (for all but the very smallest value of σ^*) but larger than that in the parabolic decay region. On this basis, grafted layer dominance in the uniform layer region and mobile chain dominant behavior in the parabolic decay region would be expected. No scaling relation is evident between σ^* and d_u or σ^* and $(d_t - d_u)$, indeed the situation (modest molecular weight graft polymer which is much smaller than the mobile polymer) is considerably different compared from that defined by de Gennes in developing the scaling relations above. For the uniform layer region, its thickness for the copolymer film spread on the 5% PEO solution has about half the thickness of the grafted PEO layer when spread on the 0.1% and 2% PEO subphases, and these in their turn are about half the uniform layer thickness when the copolymer is spread on pure water. In a like manner, the concentration of ethylene oxide segments (as quantified by their number density) in the uniform layer region of the copolymer film spread on the 5% PEO subphase is larger than that for the film spread on the 0.1% and 2% PEO subphases, i.e., the increased concentration of PEO in the subphase has led to a densification and compression of the uniform layer region of the poly(ethylene oxide) grafts in the subphase. We note, however, that there is no increase in the number density of the uniform layer relative to that for the copolymer spread on water alone. The number density of ethylene oxide segments in the uniform layer for the 5% PEO w/v subphase is the same as that at the highest surface concentration of spread film on water.

For the region where the graft PEO segments adopt a parabolic distribution, there is no evidence of densification of

the layer due to the dissolved PEO. However the magnitude of $(d_t - d_u)$ has a weak dependence on the PEO subphase concentration, becoming somewhat larger as the subphase concentration increases. In this region the concentration of grafted PEO segments is reduced in comparison to that observed for the copolymer film spread on pure water, but the mobile PEO concentration in this region is not sufficiently high to screen excluded volume interactions between grafts and between grafts and mobile chains. Thus rather than a compression of layer thickness and densification in terms of number density of grafted EO segments, the values of $(d_t - d_u)$ are little different from those observed in the absence of dissolved PEO. Although the small number of values for $(d_t - d_u)$ prevents a precise value being established, the value of σ^* where $(d_t - d_u)$ attains an approximately constant value is very similar to that where the surface pressure isotherm shows the "phase transition" discussed earlier. The observation that $(d_t - d_u)/R_g \sim 2$ is the largest value observed for this copolymer, even in the absence of dissolved poly(ethylene oxide), suggests that this is the limit to the extensibility of the grafted chains set by their relatively low degree of polymerization and consequently more "rodlike" nature. This natural limit is reached at lower surface concentrations when spread on PEO solutions and suggests that the mobile polymer adsorbed at the air–water interface provides additional intermolecular excluded volume interactions in addition to those between the grafted chains themselves, and the chains are stretched to a greater extent than in the absence of mobile polymer and hence the number density of grafted chain segments is decreased in this region but the overall number density of *all* PEO segments is large, encouraging brush-like layer formation.

Conclusions

The surface pressure isotherms for the spread graft copolymer film on PEO-containing subphases show that the copolymer expels PEO from the surface excess layer. For the 0.1% w/v PEO this expulsion appears to be complete because the number density of grafted PEO segments in the subphase at which zero surface pressure is regained is identical with the concentration of dissolved PEO in the surface excess layer obtained from earlier experiments. When the subphase PEO concentration is higher, the expulsion is not complete and thus the concentration of PEO in the surface excess layer is higher and this influences the dimensions and composition of the grafted poly(ethylene oxide) layers in the subphase.

The incorporation of poly(ethylene oxide) homopolymer into the aqueous subphase on which a copolymer with poly(ethylene oxide) grafts is spread influences the dimensions and the composition of the layer formed by the grafts at the surface. This layer is composed of two regions where the distribution of grafted PEO is different. There is a region of uniform PEO density the dimensions of which are reduced compared to those obtained in the absence of free PEO, and the graft PEO concentration is increased by the presence of the free PEO but does not exceed that obtained when there is no free PEO in solution. The second region has a parabolic distribution of grafted PEO segments, and the thickness of this region increases with surface concentration of copolymer. The thickness reaches a limiting value of $2R_g$ at a lower surface concentration than observed for the copolymer spread on water. Thus the dissolved poly(ethylene oxide), rather than screening excluded volume interactions in this region, seems to provide additional interactions, and this extra stretching reduces the concentration of grafted PEO segments relative to that of the equivalent surface concentration spread film on water.

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