Surface segregation from polystyrene networks

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Abstract. We have used neutron reflectometry and carbon and neon forward recoil spectrometry to measure the surface segregation of deuterated polystyrene from a hydrogenous polystyrene network. We find that when the linear polymer is of a high molecular weight ($\sim$600 000), the surface segregated profile can be predicted by mean field theory. In these systems the segregation is a rather slow function of time, reflecting the large number of entanglements in such crosslinked mixtures. When the deuterated polystyrene is of a lower molecular weight ($\sim$100 000), the surface segregated layer does not evolve monotonically with time but the shape of the profile can be predicted by mean-field theory. However, when the network is significantly crosslinked, the linear polymer is expelled from the network.

1. Introduction

In binary fluid mixtures the surface is enriched in the component of the lower surface energy. In small molecule systems this phenomenon, known as surface segregation, is in general only effective on the length scale of one molecule. This is also true of polymer mixtures but their large molecular weight (M_w) ensures that the time and length scales are large enough to be easily accessible to experimental study. Surface segregation in films of isotopic polystyrene blends (in which one component is fully hydrogenous (h-PS) and the other, d-PS, is completely deuterated) has been the subject of much work [1–6] since scattering experiments showed that there was a small thermodynamic repulsion between the two polymers [7]. Advances in experimental techniques, such as ion beam profiling [8] and neutron reflectometry (NR) [9] have been responsible for much of the progress in such studies. Interest in such work has also been driven by a desire to understand the behaviour of polymer thin films, which may have applications in industries such as coatings, paints, and semiconductor insulators to name but three.

Early mean field theory and experiments have shown that the surface segregated layer of a polymer from a completely miscible polymer blend is about the same size as the radius of gyration of that polymer chain (i.e. one monolayer) [1, 10]. In this work we consider what happens if one of the components is a network. To what extent would deuterated polystyrene

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(d-PS) segregate from a normal polystyrene (h-PS) network in comparison to a blend of linear polymers? One could first of all suggest that there would be a slight increase in the segregation due to the fact that the system is less miscible because one of the components (the network) effectively has an infinite molecular weight. A more detailed analysis would include, in the mean field theory, terms accounting for polymer elasticity. This would imply that if polymer left the network, the network would have to compress itself. This would be energetically unfavourable and so cause the annealed surface layer to be smaller than in the binary blend. This would not however, forbid segregation since we only require a balance between the different effects. This balance is also seen in the reverse situation, where linear polystyrene diffuses into the network, causing it to stretch [11, 12].

We should also have to consider the effect of inhomegeneities in the network. Certainly, the polystyrene networks that we consider are inhomogeneous and it is also known that in inhomogeneous systems, linear polymer diffuses towards regions with fewer crosslinks [13]. Finally, since the surface can be considered as a less crosslinked region we should not be surprised if the linear polymer diffuses there. With these contradictory possibilities we cannot say, *a priori*, whether we should expect more or less segregation than with a comparable binary linear blend, and if the profile will exhibit similar 'mean-field' behaviour.

2. Experiment

2.1. Network preparation

The preparation of these networks has been discussed in detail elsewhere [14–17] and here we give only a brief outline. The polystyrene is functionalized by attaching an aminomethyl (CH_2NH_2) group to the *para* position on the aromatic ring at random points along the chain. The aminomethyl group is crosslinked by reaction with terephthaldialdehyde in toluene during the spin casting of the films. The aldehyde groups of the terephthaldialdehyde form a Schiff base with two CH_2NH_2 groups on the aromatic rings of two styrene monomers, thus crosslinking the polymer. The polystyrene is dissolved in toluene with the requisite amount of crosslinker added. The amount of terephthaldialdehyde (crosslinker) necessary is known from acid–base titration or NMR measurements of the average number of aminomethyl groups on the chain. These two procedures have been recently supported by infra-red spectrometry of the intermediate product [18].

We estimate an accuracy of $\pm 15\%$ in our measurement of the number of aminomethyl groups. Since we can measure the amount of CH_2NH_2 present, we can estimate the eventual crosslinking density N_c^{-1} because one needs two CH_2NH_2 groups for every crosslink. N_c is the average number of monomers in one strand linking two crosslinks.

This method of crosslinking ensures that any polymer present that does not have the aminomethyl group present on the chain will not be crosslinked but will be embedded (yet still will be mobile) within the network [14]. We describe such chains as 'trapped'. In these experiments we create networks from aminomethylated h-PS, which is dissolved in toluene, along with the terephthaldialdehyde and linear (unfunctionalized) monodisperse d-PS. A film is created by spin coating the solution onto a silicon wafer. As the solvent evaporates during the spin coating process, the gel point is passed and the network forms. When enough solvent has evaporated, the polystyrene vitrifies. After measuring the surface segregation, we could wash the resulting film in toluene to remove all linear d-PS, as well as any remaining h-PS sol. By measuring the dry film thickness before and after washing we were able to estimate the remaining sol. The most crosslinked network that we had made, with 92 monomers per crosslink, had no sol fraction present. It is possible that the least crosslinked network, i.e. with

Table 1. The different combinations of linear polymer (of molecular weight, M_w, chain length, N_A, and volume fraction ϕ_∞) with network (with an average number of monomers between crosslinks, N_c). The measurement techniques used for each mixture are also listed along with the aim of the measurements: equilibrium profile (equ) or kinetics of segregation (kin).

System	ϕ_∞	M_w (Da), N_A	N_c	Technique	Aim
A800C207	0.116	90 000, 800	207	NR, C-FReS	equ, kin
A800C461	0.116	90 000, 800	461	NR, C-FReS	equ, kin
A5450C85	0.194	610 000, 5450	85	NR	equ
A1100C92	0.278	123 000, 1100	92	Ne-FReS	kin
A5700C92	0.278	640 000, 5700	92	Ne-FReS	kin

the most (461) monomers per crosslink finished crosslinking during annealing. However, even in these films, the amount of initial sol present is still quite small (<10%). The films were annealed under vacuum above the glass transition temperature of polystyrene ($T_g = 373$ K). On removal from the oven, the surface profile is 'frozen in' and can easily be measured. The different mixtures of linear polymer in network used in this study are listed in table 1.

2.2. Depth profiling: neutron reflectometry and ion beam profiling

Experimentally, one measures the concentration of linear polymer as a function of depth into the film. For both ion beam profiling and neutron reflectometry, the deuteration of the linear polymer provides the necessary contrast with the network. The neutron reflection experiments were performed on the EROS and CRISP time-of-flight reflectometers on the Orphée reactor at the Laboratoire Léon Brillouin and the ISIS pulsed neutron source at the Rutherford Appleton Laboratory respectively. The depth profiles were obtained using a downhill simplex fitting routine [19]. Ion beam experiments were performed using the 2.5 and 7.5 MV van de Graaff accelerators at the Universities of Paris VII and VI and the University of Freiburg respectively. Ion beam experiments do not have the sub-nm resolution of neutron reflectometry but impressive resolution (better than 10 nm FWHM) can be achieved by performing FReS (often known as elastic recoil detection or ERD) with heavier ions than the helium normally used in such experiments. We used incident ion beams of 2.3 MeV C^+ [19] and 4.0 MeV Ne^{2+} [21].

3. Theory

Simple mean field theory has been rather successful in providing a good (if not perfect) estimate of the shape of the depth profile of a binary polymer film in the vicinity of the surface [2]. In a film containing a binary polymer mixture, Schmidt and Binder [10] give the depth profile near the surface by

$$z(\phi) = a \int_\phi^{\phi_1} \frac{\mathrm{d}\phi}{\sqrt{24\phi(1-\phi)(\Delta F(\phi) - \Delta F(\phi_\infty) - (\phi - \phi_\infty)\Delta\mu_\infty)}} \tag{1}$$

and the surface excess (adsorbed amount) by the integrated area under the depth profile,

$$z^* = a \int_{\phi_\infty}^{\phi_1} \frac{(\phi - \phi_\infty)\,\mathrm{d}\phi}{\sqrt{24\phi(1-\phi)(\Delta F(\phi) - \Delta F(\phi_\infty) - (\phi - \phi_\infty)\Delta\mu_\infty)}} \tag{2}$$

where ϕ is the fractional volume occupied by linear polymer, $\Delta\mu_\infty$ is the bulk chemical potential, ϕ_1 is the surface volume fraction of linear polymer and a is the statistical segment length (6.7 Å for polystyrene). Since one component is a network, the system can only be partially miscible at best. Here we shall consider the strong segregation limit of the random phase approximation because the chain length of the linear polymers, is greater than the number

of monomers per crosslink in the network ($N_A > N_c$). We know that, in equilibrium, these networks only accept a few per cent of such linear chains [14, 15], and this is also the case for other kinds of network [22]. (In the weak segregation limit the factor 24 would be replaced by 36.) In practice, the use of the strong segregation limit makes little difference to our results.

One can also calculate the surface energy difference between the linear polymer and the network from the measured surface volume fraction. Such a calculation will enable a comparison between linear polymer mixtures that is independent of the degree of immiscibility and bulk volume fraction. To do this we take a simple surface energy of the form given by Schmidt and Binder [10],

$$f_s(\phi_1) = -\mu_1\phi_1 - \frac{s\phi_1^2}{2} \tag{3}$$

where μ_1 is a surface chemical potential and $s/2$ represents the surface enthalpic reaction (a surface interaction parameter). A simple formulation of the surface energy difference has been given previously [23],

$$\Delta\gamma = \frac{k_B T}{b^3}\left(\mu_1 - \frac{b\chi}{2}\right) \tag{4}$$

where b is the lattice size, k_B is Boltzmann's constant, T is the absolute temperature, and χ is the Flory–Huggins monomer–monomer interaction parameter. The value of $\Delta\gamma$ can then be obtained from the following equation [1, 10, 23]

$$\frac{b^3\Delta\gamma}{k_B T} - b\chi(\phi_1 - \tfrac{1}{2}) = a\sqrt{\frac{F(\phi_1) - F(\phi_\infty) - (\phi_1 - \phi_\infty)\Delta\mu_\infty}{6\phi_1(1 - \phi_1)}} \tag{5}$$

where the factor 6 in the square root replaced the usual 9 to take account of the strong segregation limit.

The theory has been improved upon by including surface entropy terms [6, 24], for example, and also the surface profile of isotropic polystyrene blends has also been considered using a self-consistent mean-field theory calculation [25]. However, in this work only a qualitative theory is necessary because of the weaknesses and uncertainties in the elastic term in the free energy [26], which we discuss below.

Another complication occurs in the case of film swelling; it is unclear whether we should formulate the free energy of the network in terms of one-dimensional or three-dimensional swelling. A surface segregation experiment would imply 1D swelling but since heterogeneities may play a role [15, 16], it is also worth considering 3D swelling because some regions may swell at the expense of others. The free energies are presented as a generalization of the Flory–Wall equation [27] and given as follows

$$\Delta F_1 = \frac{\phi}{N_A}\ln\phi + \phi(1 - \phi)\chi + \alpha\frac{(1 - \phi)}{2N_c}\left(\frac{1}{(1 - \phi)^2} - 1 + \beta\ln(1 - \phi)\right) \tag{6}$$

$$\Delta F_3 = \frac{\phi}{N_A}\ln\phi + \phi(1 - \phi)\chi + \alpha\frac{(1 - \phi)}{2N_c}(3(1 - \phi)^{-2/3} - 3 + \beta\ln(1 - \phi)) \tag{7}$$

where the subscripts 1 and 3 refer to 1D and 3D swelling respectively. We are considering a functionality of $f = 4$. If we set the numerical constants, α and β to unity, this corresponds to the Flory–Rehner theory of network swelling.

We also consider the phantom network model as postulated by James and Guth [28]. In this case $\alpha = 1 - 2/f = 0.5$ [29] and we choose the extreme option where the logarithmic term inside the parentheses is removed ($\beta = 0$). The difference between the two models is that in the phantom theory one considers a network in which the crosslinking junctions are allowed to fluctuate about their mean position in space. This is not allowed in the Flory–Rehner theory.

However, it has been theoretically [30] and experimentally [31] demonstrated that the simple addition of the entropic and elastic terms used in both the Flory–Rehner and phantom theories to form the free energy of a network is not viable. Nevertheless, due to the inherent simplicity of the two models, the debate over which of them better describes the elastomeric state still continues [26].

In a partially miscible binary polymer blend, equations (1) and (2) are not applicable in the two-phase region. When one component is a polymer network the system is never completely miscible, and there will always be a minimum value of ϕ, above which the mixture can phase separate. Using the above simple forms of the free energy, the term $\Delta F(\phi) - \Delta F(\phi_\infty) - (\phi - \phi_\infty)\Delta\mu_\infty$ in the denominator of equations (1) and (2) must remain positive. This means that we are able to predict the surface profile even for partially miscible mixtures, but we cannot consider films in the unstable region.

4. Results

We performed experiments with the aim of elucidating the equilibrium profile, as well as the kinetics of segregation. In table 1, along with the various polymer mixtures used, we list the techniques used to measure them and whether the data were used to describe the equilibrium profile, the kinetics of segregation, or both.

4.1. Surface energy difference

Although the resolution of carbon or heavy ion FReS is excellent for an ion beam technique, it is still incapable of accurately resolving the volume fractions of the components at the surface. Neutron reflectometry can provide this information, which is necessary for the mean field calculations of the depth profile and surface excess (equations (1) and (2)). We measured the surface profile using neutron reflectometry for three systems annealed at ~433 K: A5450C85, A800C207 and A800C461 (the systems are fully listed in table 1). We show sample data and fits for each of these networks in figure 1, and the corresponding depth profiles in figure 2.
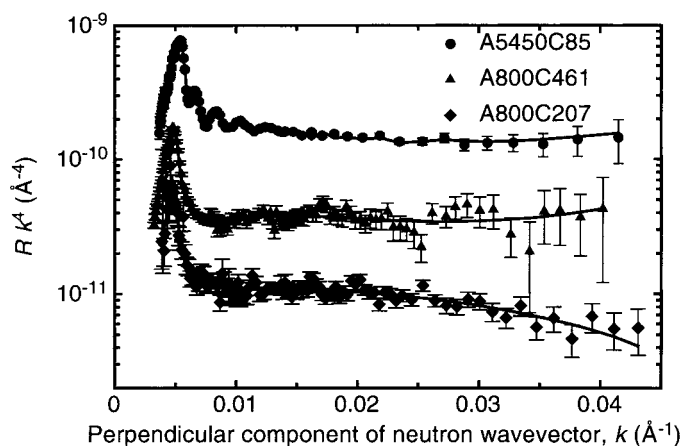
Figure 1. Neutron reflection data and fits for samples A5450C85 after annealing for 57 hours at 443 ± 1 K, A800C207 and A800C461 (both annealed for 64 hours at 443 ± 2 K). The respective values of χ^2 for the fits are 2.9, 0.8 and 1.4. For clarity, the data for the $N_c = 461$ and $N_c = 207$ networks are staggered by factors of three and nine respectively.
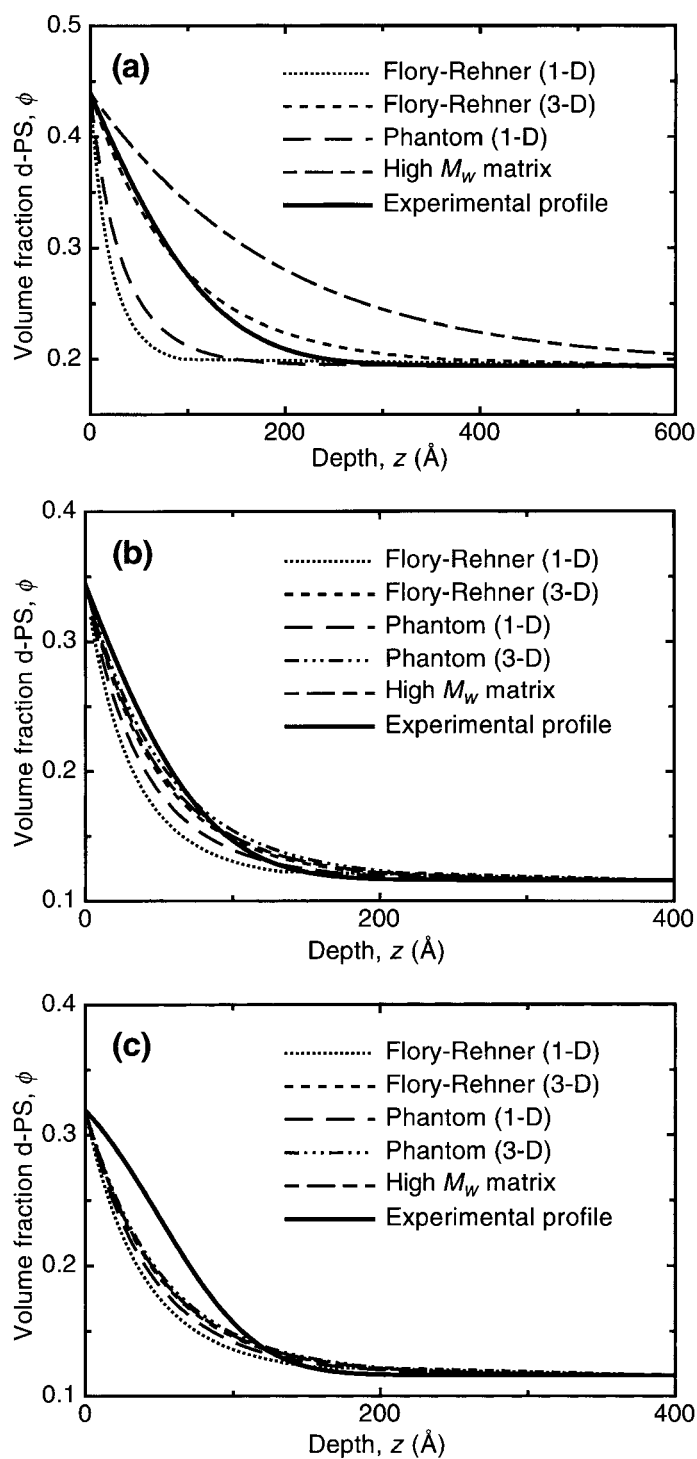
Figure 2. Theoretical and experimental equilibrium profiles obtained from the fits shown in figure 1 for samples (a) A5450C85, (b) A800C207 and (c) A800C461. The theoretical profiles shown are for the Flory–Rehner and phantom network theory in both one and three dimensions as well as an equivalent linear blend with a matrix of chain length $N_B = 100\,000$.

From the measured surface volume fractions and equation (5), we obtain $\Delta\gamma = 0.14 \pm 0.02$, 0.27 ± 0.03 and 0.24 ± 0.03 mJ m^{-2} for the surface energy differences between the linear polymer and the network for the A5450C85, A800C207 and A800C461 binary mixtures respectively (using the Flory–Rehner theory with a three-dimensional swelling term in the free energy). The trend of these results is as expected; one would expect the value of $\Delta\gamma$ to be smallest for A5450C85 because the surface energy is known to increase with linear polymer molecular weight [29]. The values are all of the same order of magnitude as those from blends of linear isotopic polystyrene. A neutron reflection study by Geoghegan and co-workers revealed $\Delta\gamma = 0.11 \pm 0.02$ mJ m^{-2} for a d-PS/h-PS blend with molecular weights of 1 030 000 (N_A, $N_B \approx 9500$) for both polymers [3]. Our values are therefore very plausible.

We can also compare the above results with our carbon FReS measurements. With carbon FReS the resolution is not good enough to extract the surface volume fraction but we can use equations (1) and (2) to estimate it from the surface excess obtained from the carbon FReS measurements. This has been done for two systems (A800C207 and A800C461) and the carbon FReS results reveal surface energy differences of 0.12 mJ m^{-2} (A800C461) and 0.24 mJ m^{-2} (A800C207). The carbon FReS result is thus consistent with the reflectometry result for A800C207 but there is a considerable discrepancy with the result for the A800C461 system.

We also note a temperature effect. Carbon FReS measurements on these blends annealed for 48 hours at the higher temperature of 454 K show that the surface energy difference rises by about 35 and 40% to 0.16 mJ m^{-2} (A800C461) and 0.33 mJ m^{-2} (A800C207). This is in keeping with carbon FReS results for four isotopic mixtures of polystyrene homopolymers, in which $\Delta\gamma$ increased by between 9% and 46% on a temperature increase from 433 K to 453 K [20].

4.2. Kinetics

To complement the above measurements of $\Delta\gamma$, we considered the kinetics of segregation using Ne-FReS on two further blends, A1100C92 and A5700C92. Sample data for the A5700C92 system are shown in figure 3. In these experiments we see that the higher N_A polymer segregates much more slowly to the surface than that with $N_A = 1100$. This is illustrated in figure 4 by the growth of the surface excess with time. We also observed in the A800C207 and A800C461 mixtures a rearrangement of the surface, resulting at latter times in a slight decrease in the surface excess with time. This we discuss at the end of the next section.

5. Discussion

### 5.1. Local equilibrium assumption

In section 4.1, we discussed at some length the measurement of $\Delta\gamma$ from the NR and carbon FReS data. We address here the question of whether or not the samples are at equilibrium. Carbon FReS data of the A800C207 mixtures (figure 5) reveal a small depletion in d-PS from the bulk value behind the surface layer after annealing at 4 hours (figure 5(b)) at 452 K. Since we can fit to our NR data without needing to invoke a depletion layer in the profile, we believe that the height of any depletion layer is not too far away from the bulk volume fraction.

Although the existence of a depletion layer suggests that the film has not reached equilibrium, this need not affect our measurements of $\Delta\gamma$ if the local equilibrium assumption
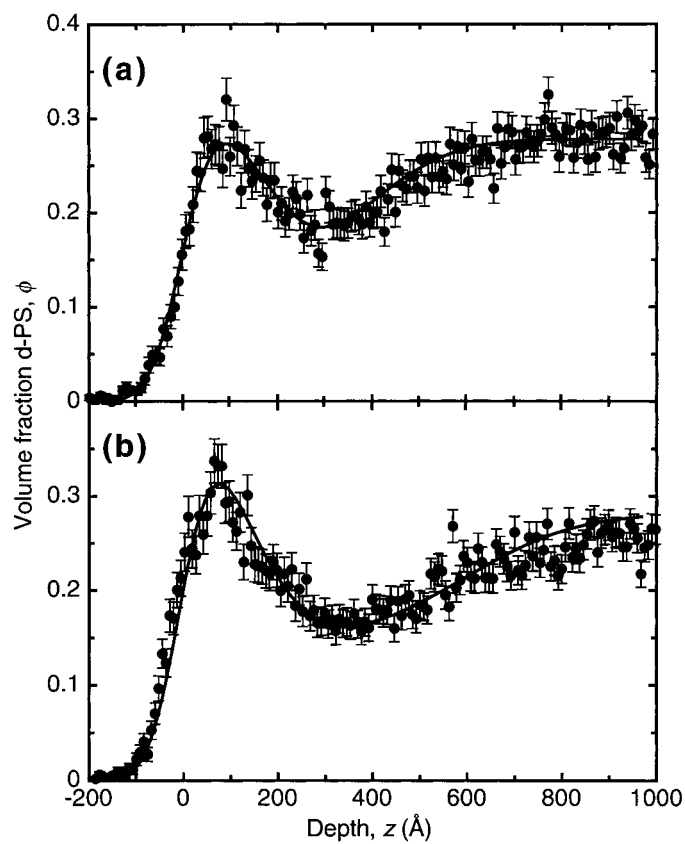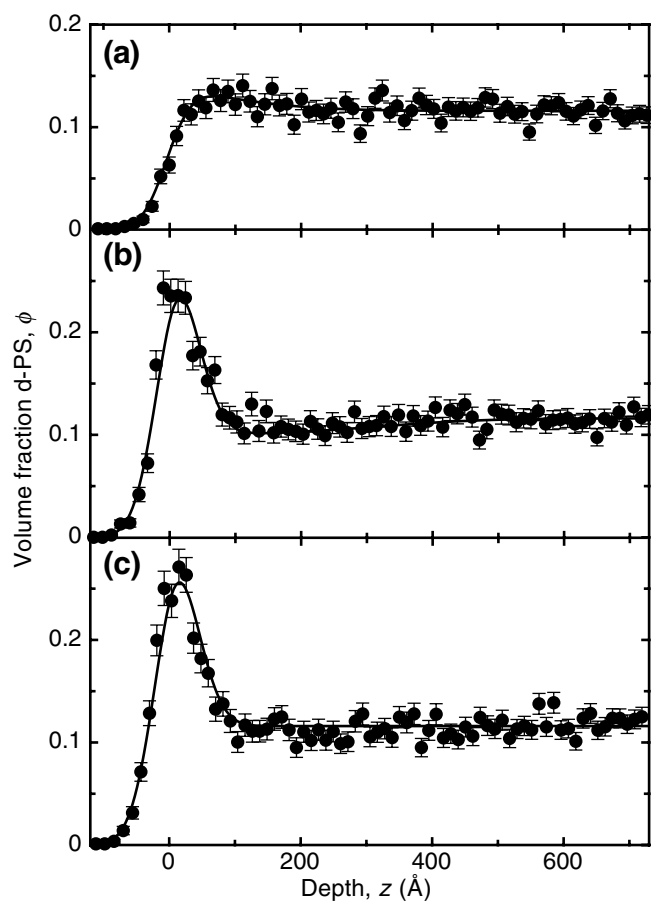
Figure 3. Ne-FReS data for the sample A5700C92. The profile in (a) is for an unannealed film and that in (b) is for a film annealed for 263 hours at 457 ± 1 K.
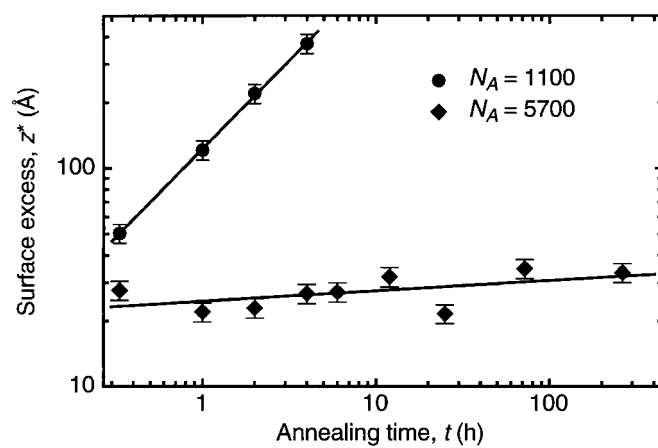
Figure 4. Surface excess as a function of time (at 457 ± 1 K) for the mixtures A1100C92 and A5700C92, as measured by Ne-FReS. The power law exponents are 0.8 ($N_A = 1100$) and 0.05 ($N_A = 5700$).

Figure 5. C-FReS data and fits for sample A800C207, after annealing for 4 hours at 452 K (b) and 48 hours at 454 K (c). In (a) we show the data and fit for the unannealed sample. In (b) a small depletion layer is visible behind the surface segregated layer, which shows that equilibrium has not been reached. In (c) this depletion layer is no longer present, indicating equilibrium.

applies [33]. Here, we assume that the surface layer is in local equilibrium with the depletion layer, i.e. the volume fraction in the depletion layer plays the role of ϕ_∞. We used the neon FReS measurements of the A5700C92 mixture (figure 3) to check the local equilibrium assumption. If the surface is in equilibrium with the depletion layer behind it, $\Delta\gamma$ should be constant. Indeed, we see that this is the case, with the surface energy difference varying within a narrow range of between $\Delta\gamma = 0.12 \pm 0.02$ and 0.18 ± 0.02 mJ m^{-2} for the different annealing times (see figure 6). Incidentally, since the sample annealed for only 20 minutes has a surface energy difference similar to the others, it is likely that such local equilibrium is rapidly attained.

5.2. Shape of the profile

We have demonstrated that the local equilibrium assumption for segregation is valid and that the value of $\Delta\gamma$ is in good agreement with measurements on polymer blends. However, this suggests that the fact that one component is crosslinked is of only minimal importance. To test
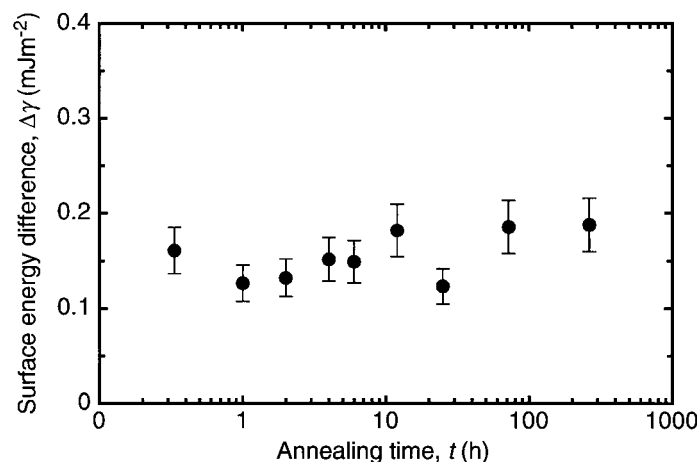
Figure 6. The measured surface energy difference, $\Delta\gamma$ between a d-PS linear polymer ($N_A = 5700$) and an h-PS network ($N_c = 85$) at 457 K is plotted as a function of annealing time. The surface energy difference was calculated from Ne-FReS data using the Flory–Rehner theory with three-dimensional swelling.

the effect of crosslinking on the equilibrium profile, we extend our analysis to the shape of the surface profile as measured by NR. For the mean field prediction (equations (1) and (2)), we use a Flory–Huggins interaction parameter given by [7]

$$\chi = \frac{0.2}{T} - 0.000\,29 \tag{8}$$

where we assume a lattice parameter based upon the density of one monomer.

These equilibrium and theoretical profiles are shown in figure 2. In considering the theoretical mean-field profiles, the effect of crosslinking is only noticeable in the most crosslinked, largest N_A system; only in this case does theory predict a significant difference between a high M_w linear polymer matrix and a network matrix (figure 2(a)). For this most crosslinked system, the agreement between the simple Flory–Rehner mean-field theory comprising 3D swelling is very good. The phantom network prediction of James and Guth (3D swelling) could not predict the surface profile for this mixture (the terms in the roots of equations (1) and (2) were negative; this theory predicts that the mixture is no longer miscible) and so no such profile is shown in figure 2(a). The one-dimensional case predicts less segregation and the agreement is less impressive. The lower molecular weight d-PS ($N_A = 800$) also shows better agreement with the three-dimensional swelling (both Flory–Rehner and the phantom theory) than with 1D swelling but in the case of $N_c = 461$, the agreement is not so good. The reason for this poorer agreement in the least crosslinked mixture is not clear but may well be related to the distribution of heterogeneities.

We postulated earlier in the article about the surface behaving as the least crosslinked region and so linear polymer would preferentially segregate to it. In the light of these results, this is unlikely, as we should expect a surface volume fraction of unity with this hypothesis. One could also suppose that the linear polymer does not leave the film, except to form isolated droplets at the surface. This is possible but even so, one would expect the roughness to be greater than the 5 to 12 Å which we measured with NR. This roughness is typical for a homogeneous film of polystyrene.

In summary, from our results we conclude that the size of the surface layer is in qualitative agreement with mean-field theory. Mean-field theory describes the balance between expulsion and entropic mixing well, at least for the values of N_A and N_c that we discuss. We shall now see that the kinetics is much slower than expected and that there is also some subtle behaviour due to relaxation of the network.

5.3. Kinetics of segregation

Here we consider the evolution of the surface profile as a function of annealing time. This evolution does not start from a homogeneous profile because we observe an enrichment or depletion in d-PS linear polymer at the surface in unannealed films (as in figures 3(a) and 5(a)). In measuring the surface excess as a function of time, a power law time dependence, $z^* = (at + t')^n$, will be considered, where the t' term accounts for the segregation in the unannealed sample.

5.3.1. Diffusion coefficients.
FReS measurements of the kinetics of segregation in isotopic blends of linear polystyrene has shown that the surface segregated layer should equilibrate after a time of order [5]

$$t_{eq} = \left(\frac{z_{eq}^*}{\phi_\infty} \right)^2 \frac{1}{D} \tag{9}$$

where z_{eq}^* is the equilibrium surface excess and D is the interdiffusion coefficient. This kinetic behaviour has been qualitatively confirmed in separate neutron reflection experiments [3]. We can make a comparison between interdiffusion and surface segregation measurements using the carbon FReS results for A800C207 (figure 5). This blend had not reached equilibrium after 4 hours annealing at 452 K with a surface excess, $z^* = 12.7$ Å. After 48 hours annealing at 454 K, the depletion layer was no longer visible and we can assume the sample was at equilibrium ($z^* = 14.0$ Å). From equation (9) we estimate an interdiffusion coefficient in the range of 10^{-16} to 10^{-17} cm^2 s^{-1}. We can compare the values of D obtained from the data here with direct measurements of D^*, the intradiffusion coefficient (Brownian motion) of this d-PS ($N_A = 800$) in the same network ($N_c = 207$) measured by ^{3}He nuclear reaction analysis [12]. To compare D^* with D, we have to scale it from 423 K to 454 K using Williams–Landel–Ferry theory [34]. This gives an intradiffusion coefficient some $\sim10^4$ times larger than the interdiffusion coefficient referred to above. The intradiffusion coefficient in partially miscible blends is usually only slightly greater than the interdiffusion coefficient due to enthalpic effects. In networks however, such effects are hard to quantify and are considered in a further detailed study [12].

5.3.2. Comparison with a blend.
Carbon FReS measurements [20] on the surface segregation of $\phi_\infty = 0.231$ d-PS ($N_A = 5450$) from a matrix of linear h-PS ($N_B = 13\,900$) show an equilibrium surface excess of 46 Å after 120 hours at both 433 and 453 K. This is considerably more than our neutron reflection results whereby a surface excess of 20 Å (using the same d-PS linear polymer with $\phi_\infty = 0.194$) was obtained after 57 hours at 443 K ($N_c = 85$). It could be that this film has not reached equilibrium because the large M_w of the linear polymer means that the approach to equilibrium is very slow. The terminal time of a polymer chain trapped in entanglements fixed or otherwise, is inversely proportional to the density of entanglements. In a polystyrene melt, this is $N_{ent} = 170$. The total entanglement density is given by

$$\frac{1}{N_{rep}} = \frac{1}{N_{ent}} + \frac{1}{N_c} \tag{10}$$

which, for our mixture, gives $N_{rep} = 57$, a factor of three more densely entangled than in a melt of linear chains. The translational diffusion coefficient (inversely proportional to the terminal time) is thus lowered by a factor of three. If the linear polymer finds itself entangled in more densely crosslinked regions of the heterogeneous network, this diffusion coefficient will be even lower.

5.3.3. The effect of molecular weight on the kinetics. We plot the surface excess from the above measurements of A5700C92 as well as A1100C92 (figure 4). In both cases the mixtures should be unstable regardless of whether the Flory–Rehner or the phantom network model is used. In the case of the higher molecular weight linear polymer, the growth of the surface layer was very slow, suggesting that segregation is inhibited by either entanglements or (and) a large activation energy barrier to polymer motion. The activation energy can be explained by the trapping of the chains in regions with fewer crosslinks. In the case of A1100C92, segregation was rapid and dramatic. The growth for the first four annealing times (to 4 hours at 457 K) was $t^{0.8}$ and after this time the segregation penetrated a distance of greater than 100 nm (the measurable depth using Ne-FReS in our sample geometry) meaning that the surface excess was no longer measurable. We note from these measurements that the d-PS ($N_A = 1100$) was completely expelled from the network.

5.4. Rearrangements at the surface: evidence for a two-stage process

When considering the profiles obtained by neutron reflectometry for the segregation at $\sim$433 K of d-PS of A800C207 and A800C461, we noticed that, for the latter mixture, the amount of segregation after 64 hours (15 Å) is actually *less* than that after 4 hours (13 Å). Similarly for A800C207, the amount of segregation at 64 hours (12 Å) is less than that after 16 hours (33 Å). This was also observed in carbon FReS measurements on the A800C461 mixture after annealing at 453 K. There was less segregation after 48 hours (6 Å) than 4 hours (9 Å). (This was not observed with A800C207.)

A perhaps-related effect has been observed with linear polystyrene placed in contact with polystyrene networks [17]. Linear polymer initially crossed the interface and entered the network, but after a certain time, the amount of linear polymer that had crossed the interface actually decreased. In that paper, we proposed that the polymer, in a first stage, had swollen the regions of the networks with fewer crosslinks and eventually, in a second stage, relaxed by expelling the linear polymer into the bulk of the network. This may be observed when relaxation times are comparable to the experimental time scales. The surface segregation is therefore a two-stage process.

We speculate then, that the first stage of the swelling is via the least crosslinked regions. These have a larger tube diameter than other regions and so diffusion is expected to be faster. Having reached the surface, these regions with fewer crosslinks will be swollen much more than the other regions at the surface. More densely crosslinked regions will be either compressed or simply forced away from the surface. These movements of large-scale heterogeneities will have their own very long time scales. Such compression of crosslinked regions is unlikely to correspond to equilibrium and so linear polymer may diffuse from the swollen, less crosslinked regions to these more crosslinked regions. Since there is less surface segregation in more crosslinked networks (figures 2(b) and 2(c)), this may be due to a resultant net flow of linear polymer away from the surface, which was initially swollen because it acted as a region with fewer crosslinks.

6. Summary

We have used high-resolution ion beam profiling techniques to measure the adsorbed amount of linear polymer from a polymer network to the vacuum interface as a function of time. We have also used neutron reflectivity to measure the shape of the surface profile. The equilibrium surface profile behaves in general in a similar manner to that in linear polymer blends, with simple mean-field theory providing a satisfactory prediction of the profile. Simple mean-field theory of surface segregation in a mixture of two linear polymers performs as well as the theory with swelling terms included for less immiscible systems. However, for the least miscible mixture studied, segregation was only successfully modelled by extending the theory to include three-dimensional swelling terms. The surface energy difference between the two components is of a similar magnitude to isotopic blends of linear polystyrene.

In systems whereby the network has smaller linear chains segregating from networks with a range of crosslinking densities we see evidence for relaxation effects in the networks. This leads to the counter-intuitive case whereby the segregation initially increases and then decreases. Such behaviour was observed using both neutron reflectometry and ion beam analysis. We suppose that in the case of the high-molecular-weight ($\sim$600 000) linear polymer, the reptation time for the linear polymer is longer than any network relaxation time and so such relaxation effects are not observed. An additional relaxation time was also postulated in our previous work on network interfaces [17].

In conclusion, further work should carefully correlate the spatial distribution of crosslinks and long-time kinetics with the surprising fact that mean-field theory can be so easily applied to such networks given that heterogeneities must be present.

Acknowledgments

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