A neutron reflectometry study of polystyrene network interfaces

M. Geoghegan[1,a], F. Boué[1], G. Bacri[1], A. Menelle[1], and D.G. Bucknall[2]

[1] Laboratoire Léon Brillouin (CEA-CNRS), CE-Saclay, 91191 Gif-sur-Yvette Cedex, France
[2] The Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK

Abstract. We have used neutron reflectometry to measure interfacial widths between two polystyrene films, where either one or both films are crosslinked. The observed interfacial width between two networks is larger than the size expected for "dangling ends", which suggests motion of heterogeneous regions of the networks. In the case when one of the networks is replaced by a linear polymer, the interfacial profile can be asymmetric with a diffusion "front" of linear polymer penetrating the network to a length scale of up to 200 Å. In the case of a more densely crosslinked network and a high molecular weight linear polymer the interface is symmetric implying negligible penetration.

PACS. 68.35.Ct Interface structure and roughness – 82.70.Gg Gels and sols

1 Introduction

Polymer networks are very popular in many industrial processes due to their strength and malleability. Their existence in many natural forms also makes them of scientific interest. The study of polymer surfaces and interfaces is a relatively new field, and has become possible due to the explosion in the number of techniques capable of giving information about polymer interfaces in the past ten years. There are many motivations driving forward research in this field, for example, the desire to improve coatings or for other forms of surface modification. Since little attention has so far been paid to the case where one component is a network, there is a clear desire to further our knowledge about their behaviour.

Measurements of interfacial widths between polymer films is one method of obtaining knowledge of the properties of the interfaces. One important interfacial property is that of adhesion [1]. If one imagines two immiscible polymers, the size of the interface is determined by the interaction between the two polymers, the interface being sharper for more immiscible polymers [2,3]. In this case one would expect the interface between two networks or a network and a linear polymer to be sharper than that between two equivalent homopolymers due to the decrease in the entropy of mixing. However, this point of view oversimplifies the problem. Polymer networks have various properties different to those of linear polymers. They can be heterogeneous or they may be prepared in a swollen state for example, and these properties can be expected to af-

fect the interfacial profile, both encouraging diffusion and increasing adhesion.

There has been some work on the interface between polymer networks and linear polymers. The interdiffusion of polystyrene into polystyrene networks has been studied [4] as has that into polystyrene networks created by radiation crosslinking [5] or by growing the network in the copolymerization of polystyrene with divinylbenzene [6]. Some of this work has been on the interdiffusion process [4,5] and the other [6] noted a cut-off molecular weight of linear d-PS, above which no further diffusion into the network takes place. Tracer diffusion inside polymer networks has also been described [4,7]. Other than this work with polystyrene, experiments have been performed on the swelling of polydimethylsiloxane (PDMS) networks with brushes of PDMS [8]. The amount of such data is limited by the difficulty in making these networks. For reflectivity experiments they must be flat, for example. They also should be of a known crosslinking density if any serious comparison with theory is to be attempted. There must also be negligible sol fraction. This last point is a weakness in many preparation methods, but fortunately is not one which affects the method used in this work. Theoretically, however, work has focused on the strengthening of such interfaces by the use of "connector" molecules [9] (these connector molecules may be either added to the rubber in order to strengthen it or could be artefacts such as a sol component).

In this paper we shall focus our attention on interfacial width measurements involving a model system; that of polystyrene, which has the advantage of being well understood and of allowing us to make random networks of a known crosslinking density. This paper is divided up as follows: After the experimental section we turn our attention

[a] *Present address:* Fakultät für Physik, Universität Freiburg, Hermann-Herder-Straße 3, 79104 Freiburg, Germany
e-mail: `geog@frbr00.physik.uni-freiburg.de`

to neutron reflectometry measurements of the interfacial width between a deuterated polystyrene (d-PS) network and a normal (hydrogenous) polystyrene (h-PS) network. We then consider measurements of the interface between d-PS linear polymers and h-PS networks (or a h-PS linear polymer and a d-PS network). In these experiments we are considering only circumstances where there is little or no interdiffusion of the linear polymer into the bulk of the network.

2 Experimental

2.1 Synthesis of networks

The synthesis has been described previously [10–12] but we describe it again in order to highlight advantages over other crosslinking methods. The reaction is a three stage process, using a Friedel-Crafts, and then an exchange, reaction to randomly functionalise the polystyrene with an aminomethyl group, and then the crosslinking reaction.

Monodisperse polystyrene is first dissolved in distilled dichloromethane to which we add a small amount of N-chloromethylphthalimide (between 0.1 and 1 mmol per gram of polystyrene), depending on the amount of crosslinking desired. This reaction is allowed to proceed for up to four hours under argon in the presence of a catalyst ($SnCl_4$) before being stopped with a small amount of tetrahydrofuran (THF). After precipitating and drying the polymer, we dissolve it in THF and react it under reflux for between 9 and 15 hours with hydrazine (NH_2NH_2) which is dissolved in a small amount of ethanol. The polystyrene is now functionalised with an NH_2CH_2 group on the para-position of the phenyl ring at random points along the chain. It is then precipitated twice in methanol, once in the presence of a base (potassium tertbutoxide). We determine the number of aminomethyl groups by titration; 0.01 M HCl in water is titrated into a solution of the functionalised polymer in THF and water. When enough HCl has been added such that the polymer solution becomes acidic we can calculate the number of aminomethyl groups from the volume equivalent of titrated HCl. We crosslink the polymer using terephthaldialdehyde. This crosslinker is added to the polystyrene solution just before we spin cast the film and crosslinking takes place during the spin casting process. The crosslink has a functionality of four. We can verify that the films have crosslinked by simply dropping toluene on a film floating on water. Uncrosslinked films break up easily; the networks remain unbroken when the toluene has evaporated. We do not know to what level the reaction has completed so it is possible that further crosslinking takes place during annealing, especially at the temperatures used in this work.

The crosslinking is expected to be a truly random process because the existence of a crosslink on one site is not expected to encourage or hinder crosslinking from taking place at nearby sites [10]. As in any random system there will be dense regions and sparse regions and these heterogeneities can have profound effects on the properties of the network. Here we shall often refer to the less

crosslinked regions as "soft" regions. These heterogeneities are only visible if the network is somehow perturbed by either stretching (this leads to the well known "butterfly patterns" [12,13]) or swelling [13,14].

The crosslink described above is a bulky crosslink and is not expected to be neutral to linear polystyrene chains. This is also more or less true for other crosslinking techniques, however. With the method described above there is no chain scission (a problem affecting networks created by radiation crosslinking) and the distribution of crosslinks is random, and not influenced by, for example, aggregation during a copolymerization process. Finally we do not need to indirectly measure the crosslinking density by looking at, say, equilibrium swelling ratios which require a knowledge of the crosslink distribution.

The samples were prepared by spin coating polystyrene films or networks onto a silicon substrate from which the native oxide layer was not removed. Another film was spin cast onto a glass substrate. This film was floated off onto water, and the water slowly removed to allow this film to settle gently on the first film, placed below. This ensures smooth films suitable for the neutron reflectometry (NR) experiments. NR relies on deuteration for contrast, so in these experiments one component (usually the component in contact with air) was always d-PS (this gives us a greater reflectivity than in the case whereby the h-PS constitutes the upper layer). For these experiments the layers were (usually) at least 3500 Å thick in order to prevent interference fringes in the NR data. These "thickness fringes" allow one to measure the thickness of the layer, and also contain information about the interfacial width. These benefits are outweighed by the fact that one must have an excellent understanding of the resolution and its variation with wavelength; also one must have very homogenous films because thickness variations will tend to wash out the fringes, in a similar way to increasing the interfacial width or decreasing the resolution.

2.2 Neutron reflectometry

Neutron reflectometry is a very powerful method of analysing buried interfaces and has been described in detail elsewhere [15,16]. Two reflectometers were used to obtain the NR data described in this paper: the time-of-flight instruments EROS, on the Orphée reactor at the Laboratoire Léon Brillouin and CRISP, on the ISIS spallation source at the Rutherford Appleton Laboratory. The time of flight technique allows us to irradiate the sample with a range of wavelengths at the same time, minimising the number of angles necessary. On EROS data are obtained at one angle, usually 1.4°, with wavelengths in the range 3 Å to 25 Å allowing an extremely good range in neutron wavevector. In order to obtain reasonably good statistics at both higher and lower wavelengths, where the neutron flux and reflectivity respectively are significantly reduced, we were only able to perform a maximum of two samples per day (recent improvements to the neutron guide now allow three samples).

Neutron flux is not a problem on CRISP, where the synchrotron on the ISIS spallation source provides a proton current of about 200 μC hour^{-1} on the tantalum target and so two hours are enough to obtain data at three angles. Three angles are needed since we normally obtain data within a smaller range of between 2 and 6.5 Å. To account for the differing intrinsic resolutions at these three angles, the size of the collimating slits were adjusted. Interference fringes from a thin film of d-PS were used to confirm that the resolution was constant.

The data were analysed using a downhill simplex fitting technique [17]. Much has been written about different ways to analyse NR data (maximum entropy [18], simulated annealing [19] and other "exact" methods of analysing the data away from the total reflection edge (the so-called "Born approximation") [20]) but the simplex enables the user to work to a mathematical form for the profile [21]. Neutron reflection does benefit greatly from *a priori* information about the sample, often obtained in the form of ion beam data [22]. In our case ion beam data would not provide us with any supplementary information from that which we know already. This information, two polymer layers of known scattering length density on a silicon substrate, is sufficient to remove any significant ambiguities that the loss of phase information in reflection experiments causes. The simplex is also reasonably robust, and can find minima other than local minima. Like any multidimensional fitting technique, however, it will not always find the true minimum.

3 Results and discussion

3.1 The interface between two polystyrene networks

3.1.1 Results

The growth of the interfacial width between the two polymer networks with the square root of time is shown in Figure 1. In all cases these results were obtained by fitting the reflectivity to a Gaussian roughness profile; it is the Gaussian width, σ, rather than the half width at half maximum that we plot in Figure 1. This profile is the same as a complementary error function (which is the result of the convolution of a step function with a Gaussian). The fact that the profile is a complementary error function is evidence that the crosslinking process has not left behind a significant sol fraction. The latter would bring another contribution from its diffusion across the boundary, possibly creating an asymmetric profile when the two networks are different (the sol fraction is very sensitive to the crosslinking process). Networks differing significantly in their respective crosslinking density (and with no sol fraction present) may also lead, to some degree, to an asymmetric profile, and the fact that we do not actually see such asymmetric profiles is also interesting. (We define an asymmetric profile as one which is not symmetric about a 180° rotation about the centre of the interface.)

The most striking feature of Figure 1 is that the interfacial width does not vary much with time nor temperature. We note the following:
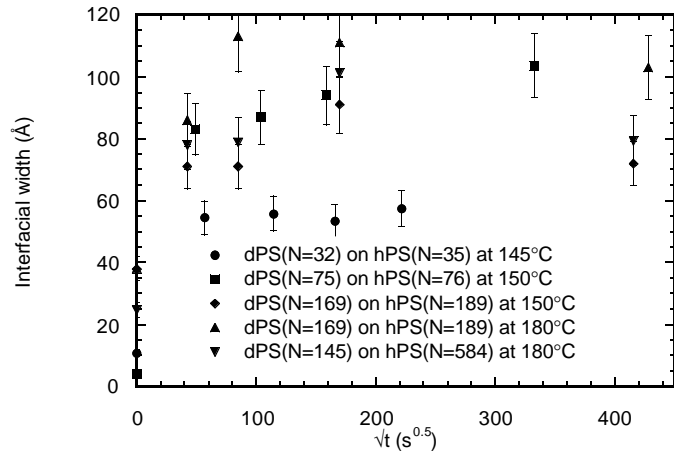

Fig. 1. The interfacial (Gaussian) widths between two polystyrene networks are plotted as a function of $\sqrt{t}$. The data for the most crosslinked bilayer were obtained during *in situ* heating. The widths for this bilayer will need a small correction for thermal expansion. A correction has been added to these data (d-PS ($N = 32$) and h-PS ($N = 35$)) to account for the fact that this set was heated at lower temperatures (115 and 130 °C) for about two days before the 145 °C measurements were made. This correction was made using the Williams-Landel-Ferry form for the polymer mobility [23].

- There is a wide variation in initial interfacial widths (or, more accurately, roughness since no interpenetration is expected to have taken place). We have seen that, in general, the more crosslinked a film is, the rougher the surface is likely to be. If we have added too much crosslinker (due to the uncertainty in the titration measurement of the number of aminomethyl groups) there may be some terephthaldialdehyde which may crystallize on the surface of the film increasing the roughness. If solvent has remained trapped in the network after the spin casting process (it is possible that densely crosslinked regions might retain some solvent), then there may be a little interpenetration across the interface.
- The width only increases with time in the first hour or so of annealing. It might be that much slower processes are involved concerning the bulk motion of heterogeneous regions in the network but we have only annealed up to about two days.
- We cannot discern any temperature dependence. Increasing the temperature could contribute by speeding up the growth of the interfaces but even this is not obvious from our data. The achievement of equilibrium also appears to be largely temperature independent.
- We see a weak dependence on crosslinking density. On one hand, the sharpest interfaces (~ 54 Å) have been obtained for the most crosslinked system ($N = 35$ for the h-PS network and $N = 32$ for the d-PS network, where N is the average number of monomers per crosslink). On the other hand, the other results show no strong correlations. For greater values of N, the interfacial width lies in the range 70-110 Å. For the asymmetric bilayer where one network has $N = 584$ (h-PS) and the other $N = 145$ (d-PS) the interface

is still around 100 Å, which suggests that the more crosslinked network controls the size of the interfacial width.

3.1.2 Discussion of the interface structure

The interface between two polymer networks can be controlled by several factors and we shall discuss these below in turn (see also Fig. 2):

1. The roughness associated with the network is expected to be controlled by the distance between crosslinking points. Thermal agitation is likely to result in parts of chains of one network crossing the interface and diffusing into the other network. This diffusion should be limited by the elastic energy of deformation of the corresponding chain and of the displacement of the junctions. From classical theories of rubber elasticity, such motion should not exceed the radius of gyration of one mesh, ~ 25 Å for $N = 100$ monomers. We can actually derive another estimate, by using an analytical expression for the free energy which we turn to later.

2. Another possibility is due to the presence of "dangling ends" in the network. The networks are not end-linked so there are expected to be chains trapped at one end by the network, and it is clear that these will be able to stretch across the network to the other side of the interface. We note that the size of these dangling ends is governed by that of the mesh on average but will be very polydisperse. The size distribution of these dangling ends will be similar to the distribution of N in the network, *i.e.* a Poisson distribution for a completely random network. Not only is this distribution unknown in these networks but we have also assumed that the quantity of branched chains which are still mobile can be neglected. In principle these branched or "decorated" chains should be small in number, due to the high number of crosslinks per chain meaning that we are well above the gel point. If dangling ends were the dominant cause of the interfacial width then the interface would probably be more Lorentzian than Gaussian (due to the polydispersity). It is doubtful whether we should be able to distinguish between the two in our experiments. We see from our data that the interface is larger than that due to just dangling ends. An interface due to just dangling ends would again have a size of the order of 25 Å for a network with $N = 100$. Each individual chain is expected to be ideal (Gaussian) and although entropy would encourage such chains to cross the boundary, should a dangling end have a tendency to cross the boundary it would have to stretch, and could no longer remain ideal (the stretching is necessary since the point where the chain is tethered to the network will be less mobile). This, and the small isotopic enthalpic repulsion of the other side of the interface, may limit the movement of dangling ends. We also note that for networks of differing crosslinking densities, an interface dominated by dangling ends would be expected to be asymmetric and we have seen no evidence for this. Nonetheless, dangling ends are expected to contribute to the interfacial widths to some degree, although not as the major component.

3. Heterogeneities in the network can increase the interfacial width. Chains trapped where the crosslinking density is low are more mobile than those in a high crosslinking density [24]. One way of considering this is to refer to the tube model of polymer chains and realise that the tube diameter is much larger in regions of low crosslinking density than in more densely crosslinked regions. This may be due to two effects (we discuss the second in the next paragraph). Firstly, we have said that these networks are random so there will be regions of low crosslinking density. It is also possible that these regions could be located preferentially at the surface for entropic reasons [25]. The tube diameter consists of two components, that of the entanglement length of the polymer and that of the density of crosslinking. The entanglement length of polystyrene is such that there is, on average, one entanglement for 170 monomers. This corresponds to an end-to-end root mean square length of about 80 Å (the tube diameter) and this value, which is related to the entanglement length is at the limit of our measured interfacial widths. In a network formed in the dry state we cannot consider sizes smaller than this length scale since these entanglements will have always been there. We can conclude that this is possibly a significant contribution to our interfacial widths but we also note that a real width, dependent on the entanglement length or tube diameter of polystyrene, is likely to be an overestimate since the tube diameter essentially represents the *entire space available* to a polymer to reptate. The width is therefore more likely to be closer to the radius of gyration of a polymer of 170 monomers (35 Å). However we remember that heterogeneities of sizes larger than an entanglement length are suspected in networks prepared close to the dry state as observed by small angle neutron scattering, under stretching or swelling [10–14].

4. Another possibility is that the network is created in the presence of a certain, unknown, amount of solvent; then the films are not in the preparation state, but in a shrunken state. The networks would then like to be swollen [26] so there could be an attempt by both networks to swell each other. If the networks were homogeneous, this would increase the average size of a mesh stretched across the boundary. They may also be heterogeneous, and then a "soft" region, for example, may be created without entanglements. However, in the next section, where we discuss the interface between a linear polymer and a network, we do not see much enlargement of the interface by the linear polymers. We therefore conclude that the network is, for the most part, formed in a state close to that of the dry state. We discuss the effect of different preparation states encouraging swelling of a dried network elsewhere [4].
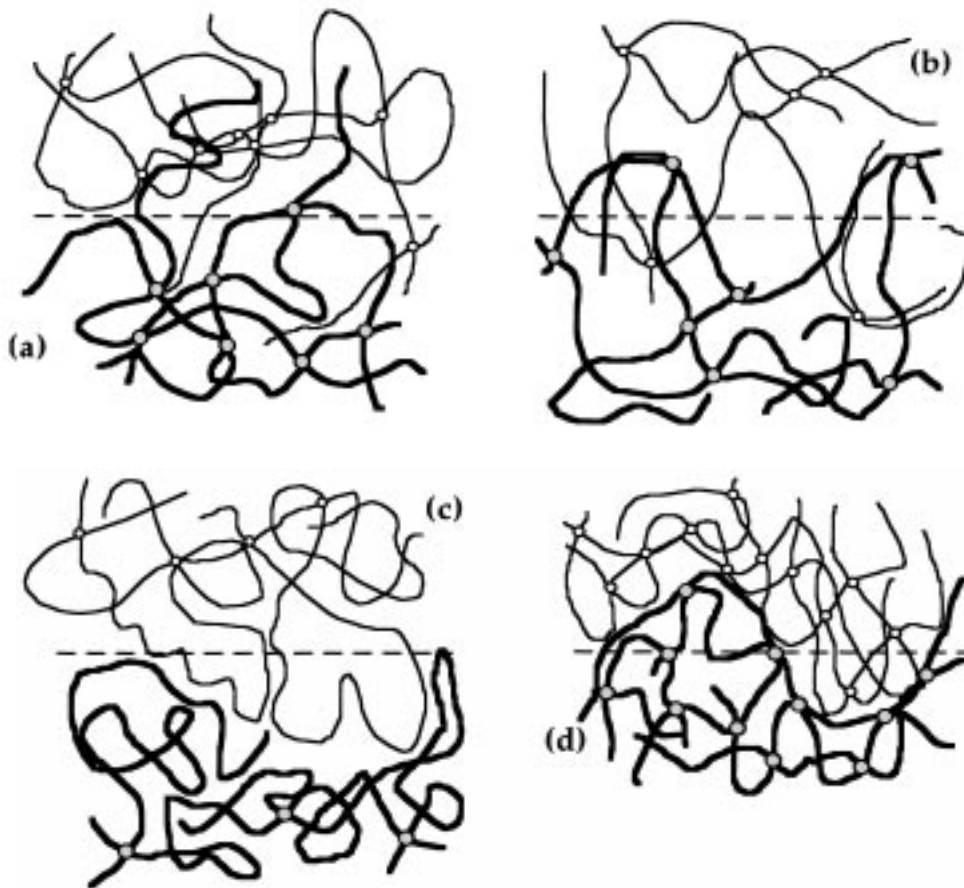
Fig. 2. Schematic of different forms of network entanglement. Crosslinks are represented by the circles, and the interface is marked by the broken line. (a) Interface dominated by "dangling ends". (b) The interface is dominated by a combination of enthalpy, entropy and elasticity resulting in an interface controlled by the mesh size. (c) The interface is formed by the swelling of one side by the other in areas where natural entanglements do not exist. Here we see heterogeneous swelling of "soft" regions. (d) Interface dominated by the elasticity due to the network. In this case the interface is "bumpy" and is much larger than the mesh size.

5. We can think of another possibility, occurring at a more macroscopic level, or at least a level where one could consider the networks behaving as a continuous elastic media. In order to eliminate the entropically undesirable sharp interface the two networks can stretch and contract to create a bumpy interface (at the expense of having a larger interfacial surface area). The controlling factor would be the elasticity of the network. More rigid (highly crosslinked) networks would have sharper interfaces than those of more supple, less crosslinked, networks. Although this form of interfacial broadening is two-dimensional (it takes place in the plane of the interface) rather than the one-dimensional penetration described in all of the above possibilities, one could not differentiate between the two using neutron reflection. If this possibility was significant, then interfacial strength measurements (in the glassy state) could show that the interface was very weak. Such work is in progress.

The third and fourth reasons discussed above are the most likely major contributions to the interfacial widths, and these should probably add by quadrature to give the total width. The fourth does not require the network to be heterogeneous. (We can neglect the significance of smaller contributions of a size similar to the mesh size, "dangling ends", for example, by a simple calculation. If we assume a typical size for the "dangling ends" as 25 Å (neglecting that this is a function of crosslinking density for this example) and that the interfacial width is about 100 Å, we have, for the width introduced by heterogeneities, 97 Å.)

We have discussed above many network specific properties that could control the interfacial width. We now return to the interfacial width based on the competition between enthalpic and entropic properties. It is worth making a comparison between two linear polymers of infinite molecular weight. Some of the possibilities that can explain an increase in the width between two polymer networks do not exist for an interface between two linear polymer films. Any immiscible system of infinite Mw will have very sharp composition gradients in comparison with the radius of gyration (since the latter is infinite) so we must assume the strong segregation limit of the random

phase approximation [27,28] in the calculation for the interfacial width of Helfand and Tagami [2] (although the use of the weak limit would not change our conclusions). For two polymers of infinite molecular weight this width, w, is given by

$$w = \frac{2a}{\sqrt{6\chi}} \qquad (1)$$

where a is the Kuhn step length (6.7 Å for polystyrene) and χ the Flory-Huggins interaction parameter [27]. The value of χ is well known for this system and is given by [29]

$$\chi = \frac{0.2}{T} - 0.00029 \qquad (2)$$

where T is the absolute temperature (we use a lattice volume of 175 Å^3). At 180 °C we calculate an interfacial width of 444 Å and at 150 °C, 405 Å [30]. Indeed, we can extend the theory for two infinite linear polymers quoted above to include the case of networks. In their discussion of the interfacial width between two immiscible homopolymers, Broseta *et al.* [3] showed that the concentration gradient at the interface is given by [31]

$$\frac{\left(w\frac{\partial\phi}{\partial z}\right)^2}{4\phi(1-\phi)} = \frac{f_{FH}(\phi)}{\chi} \qquad (3)$$

where ϕ is the volume fraction of one (the deuterated) component and $f_{FH}(\phi)$ is the Flory-Huggins free energy of mixing divided by the product of Boltzmann's constant and absolute temperature. At the interface ($\phi \approx 0.5$) we note that

$$\phi(z \approx 0) \approx \frac{1}{2} + z\frac{\partial\phi}{\partial z}. \qquad (4)$$

In order to solve equation (3) we consider the free energy of two polymer networks by adding the elastic terms from the Flory-Wall equation [32]. For a one-dimensional swelling (across the interface) we have, for the free energy,

$$f_{FH}(\phi) = \phi(1-\phi)\chi + \frac{1-\phi}{2N}\left(\frac{1}{(1-\phi)^2} - 1 + \ln(1-\phi)\right)$$
$$+ \frac{\phi}{2N}\left(\frac{1}{\phi^2} - 1 + \ln\phi\right) \qquad (5)$$

where we have used a functionality of 4 for our polystyrene network. The entropic terms usually present in the free energy disappear because the network has an infinite molecular weight but there is an entropic contribution included in the logarithmic terms, with the appropriate chain length being N (for simplicity we take equal values of N for both networks). There is much controversy over the form of the free energy [33] but we shall not go into that here as our calculations are relatively simple. Substituting (3) into (4) using (5) we obtain, for the interfacial width

$$\frac{1}{\left(\frac{\partial\phi}{\partial z}\right)(z=0, \phi=0.5)} = \frac{2w}{\sqrt{1+\frac{2}{N\chi}(3-\ln 2)}} \qquad (6)$$

which, for a network with $N = 100$ is 51 Å (at both 180 °C and 150 °C because the χ (and thus the temperature) dependence cancels out in the limit of small $N\chi$) [30]. In this limit of small $N\chi$ we have an interfacial width which scales as $\sqrt{N}$. Our measured interfaces are somewhat larger than those of this simple calculation and it seems also that the N dependence is a little weaker than $\sqrt{N}$.

We have just made a case for the temperature independence of the interfacial width between two polystyrene networks. We have seen (Fig. 1) that for a blend of $N = 169$ (d-PS) and $N = 189$ (h-PS) the interfacial width decreases from about 105 Å at 180 °C to about 80 Å at 150 °C. It is apparent that "dangling ends" (which were not specifically introduced into the above theory), for example, will stretch more across an interface at higher temperatures because the enthalpic repulsion will be smaller (a very small effect). The data that we present, however, taken as a whole, do not show any convincing temperature dependence, and so, if it exists at all, the temperature dependence is very small. The density of crosslinking is certainly more important here than any temperature dependence.

Similarly, we cannot say too much about how the interfacial width varies with crosslinking density. We note that the largest widths are generally for the bilayer with $N = 169$ (d-PS) and $N = 189$ (h-PS) (if we assume, as our data indicate, that the interfacial width is controlled by the crosslinking density of the more crosslinked polymer we do not then consider the $N = 145$ (d-PS) and $N = 584$ (h-PS) bilayer as the least crosslinked). The smallest widths are for that with $N = 32$ (d-PS) and $N = 35$ (h-PS). This means that the sample the most lightly crosslinked has the largest width and that the most heavily crosslinked, the smallest. We note that the bilayer $N = 75$ (d-PS) and $N = 76$ (h-PS) annealed at 150 °C also has a large interfacial width and so we see that the experimental uncertainty is large. One possible cause of error is overestimation of the density of crosslinking. The titration technique for determining N has an error of about 15% [10]. If we add say 15% too much crosslinker, we end up with up to 30% less crosslinks than we think we have because we have saturated the reaction (since each crosslinking molecule needs to react with two amine groups). The converse is not the same, however, if we add 15% too little crosslinker, the reaction will not be saturated and the network will crosslink to the expected degree but leaving some free aminomethyl groups. This discussion neglects the effect of uncrosslinked aminomethyl groups which may form reversible physical bonds.

3.2 Network and linear polymer

These experiments were performed with a variety of linear polymers (d-PS) and network (h-PS) sizes. The subject of the most work was when the linear polymer had a molecular weight of 920 000, for which the interfacial width was studied with networks of $N = 112$ and $N = 189$ at both 150 and 180 °C as well as with $N = 45$ at 180 °C. The network $N = 45$ was used for experiments at 180 °C with

various molecular weights (137 000, 244 000, 380 000, 610 000 and 920 000) of linear polymers. We also performed experiments at 180 °C on a d-PS network ($N = 169$) with an h-PS linear polymer ($Mw = 1\,450\,000$). The samples were, in general, annealed for the following times: 0, 0.5, 2, 8 and 48 hours at each temperature. The experiments involving the network with $N = 45$ and the experiments for samples annealed at 150 °C were performed on EROS, the others were mostly performed on CRISP. The distinction is important since the CRISP experiments consisted of a single sample per annealing time whereas those on EROS consisted of a single sample per temperature. This means that for a set of five annealing times five different samples were used on CRISP, whilst on EROS the same sample was used (after the reflection experiment, the sample was put in the vacuum oven and then the next experiment was performed and so on).

In these experiments, we observed symmetric and asymmetric interfaces. In order to account for asymmetric interfaces, we fitted to the following function;

$$\phi = 1 - \frac{1}{2}\sqrt{\left(1 + \tanh\left(\frac{x - \Delta_1}{\sigma_1}\right)\right)\left(1 + \tanh\left(\frac{x - \Delta_2}{\sigma_2}\right)\right)} \tag{7}$$

where Δ and σ are an offset and a width respectively. In the limit where $\Delta_1 = \Delta_2$ and $\sigma_1 = \sigma_2$, we recover a hyperbolic tangent profile which can be compared with the error functions that we use for symmetric profiles (if an error function was a good approximation to the interfacial profile, the fitting procedure is sensitive enough to return values of $\Delta_1 \approx \Delta_2$ and $\sigma_1 \approx \sigma_2$ even when the initial values fed into the program are for a very asymmetric profile). We only used this profile when the error function interface did not give a satisfactory value of χ^2. (With an error function there is effectively only the width as a floating parameter and so minor improvements using the asymmetric profile which has four floating parameters are not only unnecessary but undesirable.) In the case whereby the d-PS was crosslinked, a similar function was used;

$$\phi = \frac{1}{2}\sqrt{\left(1 + \tanh\left(\frac{\Delta_1 - x}{\sigma_1}\right)\right)\left(1 + \tanh\left(\frac{\Delta_2 - x}{\sigma_2}\right)\right)}. \tag{8}$$

In order to see the subtleties of the asymmetric interfaces the fits need to be of very high quality. As an example, data for one system, obtained on EROS and CRISP, are shown in Figure 3, plotted as Rk^4 against k in order to magnify the discrepancies between the data and fits. Of the data obtained, those shown in Figure 3 represent the *worst* set in terms of the quality of the fits (the volume fraction profiles are shown in Fig. 5e). This small loss in quality is possibly due to greater off-specular scattering from the d-PS network than from the equivalent h-PS networks. In the analysis of NR data one cannot extract much information separately because many of the parameters are coupled. The thickness of the deuterated film may be easily obtained if there are fringes present, the
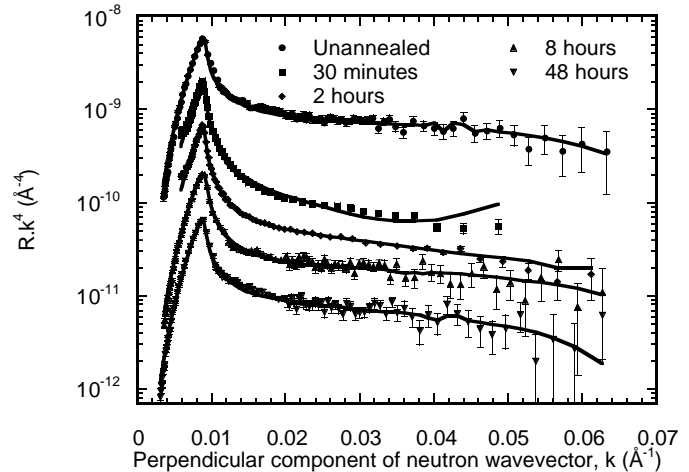

Fig. 3. Rk^4 plotted against the perpendicular component of neutron wavevector, k for bilayers consisting of a d-PS network with $N = 169$ on h-PS with $Mw = 1\,450\,000$ annealed at 180 °C for 0, 0.5, 2, 8 and 48 hours. The values of χ^2 are respectively, 6.5, 7.0, 3.4, 6.1 and 5.1. The 30 minute and 2 hour data were obtained on EROS and the others on CRISP. The unannealed data are shown as obtained whilst the data corresponding to the annealed samples are scaled by factors of 3, 9, 27 and 81 to ensure clarity.

surface roughness can be obtained by the departure from constancy of Rk^4 at high k, but the information on the shape of the depth profile is encapsulated in the reflection profile between the high k limit and the total reflection edge.

In all of these samples, except for those with the h-PS network ($N = 112$), we allowed the position of the interface to float in the fitting routine. This was necessary for those bilayers involving the network with $N = 45$ because these samples were thin enough for fringes to appear in most of the reflectivity data. However, when the d-PS layer was somewhat thicker (so that no fringes were present) there is much less control over the thickness of this layer in the fits (this does not affect the resulting interfacial profile). The variation in thickness of some d-PS layers is so large that for Figures 5c and 5e we needed to shift some of the resulting profiles by about 300 Å in either direction to avoid extending the abscissae too much. Such a variation demonstrates that the interface need not have been allowed to float because NR is insensitive to the position of the interface in these thicker films. Consequently, the profiles shown in Figures 5a and 5b were created by keeping the interface at a depth of 4000 Å and the quality of the fits would not be significantly improved by allowing the position of the interface to float.

The major problem in these experiments is one of reproducibility of the samples. Although the films with, for example, $N = 189$, are all produced from the same solution, it is not possible to ensure that each network is the same. The solution before spin casting becomes more viscous after the terephthaldialdehyde has been added due to the onset of crosslinking. This means that the first networks to be cast from a solution are slightly less viscous
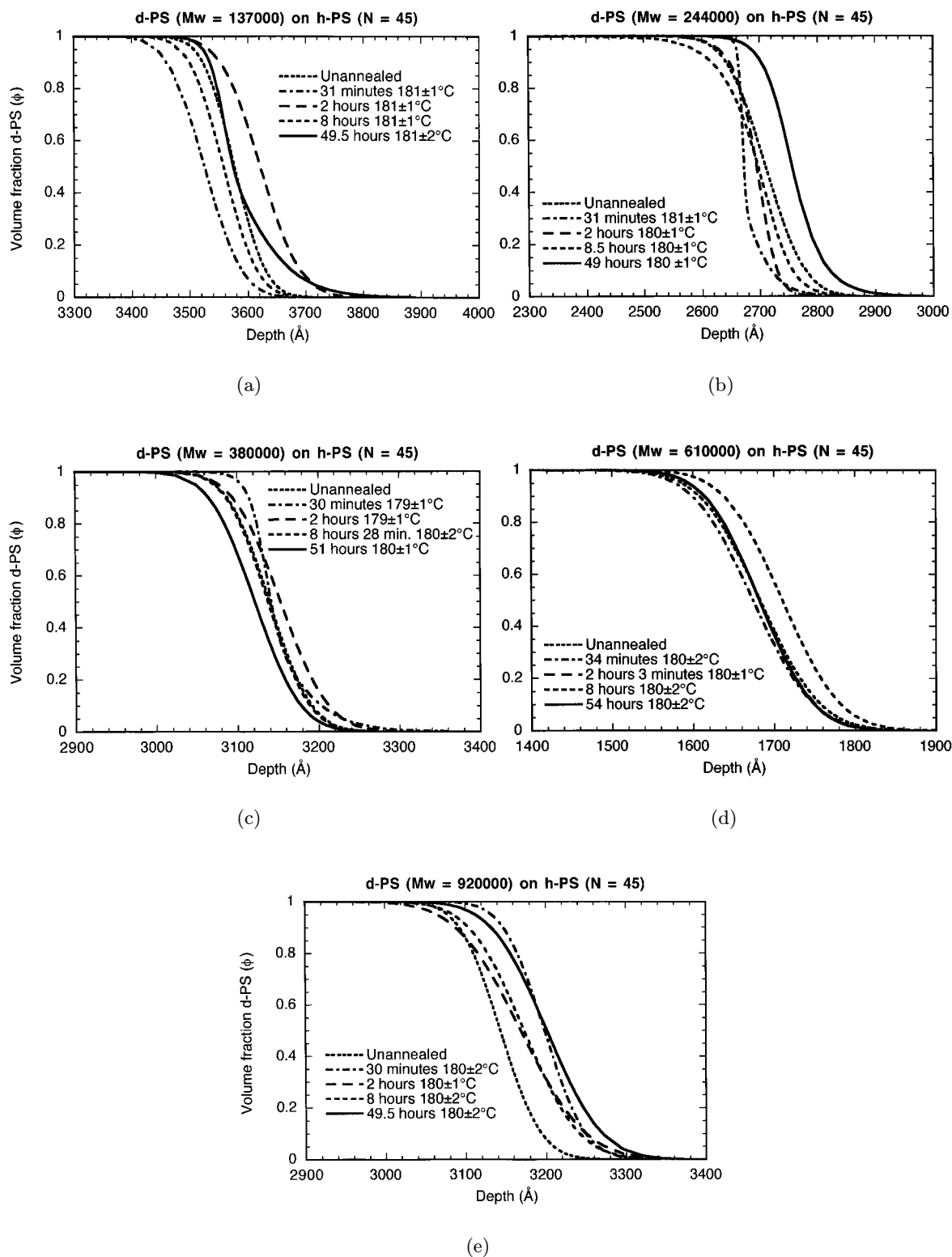
Fig. 4. Volume fraction profiles for the interfaces between linear polymers (d-PS) of $Mw = 137\,000$ (a), $244\,000$ (b), $380\,000$ (c), $610\,000$ (d) and $920\,000$ (e) and a polymer network (h-PS) with an average density of crosslinking, $N = 45$ after annealing for 0, 0.5, 2, 8 and 48 hours at 180 °C. All data were obtained using EROS.
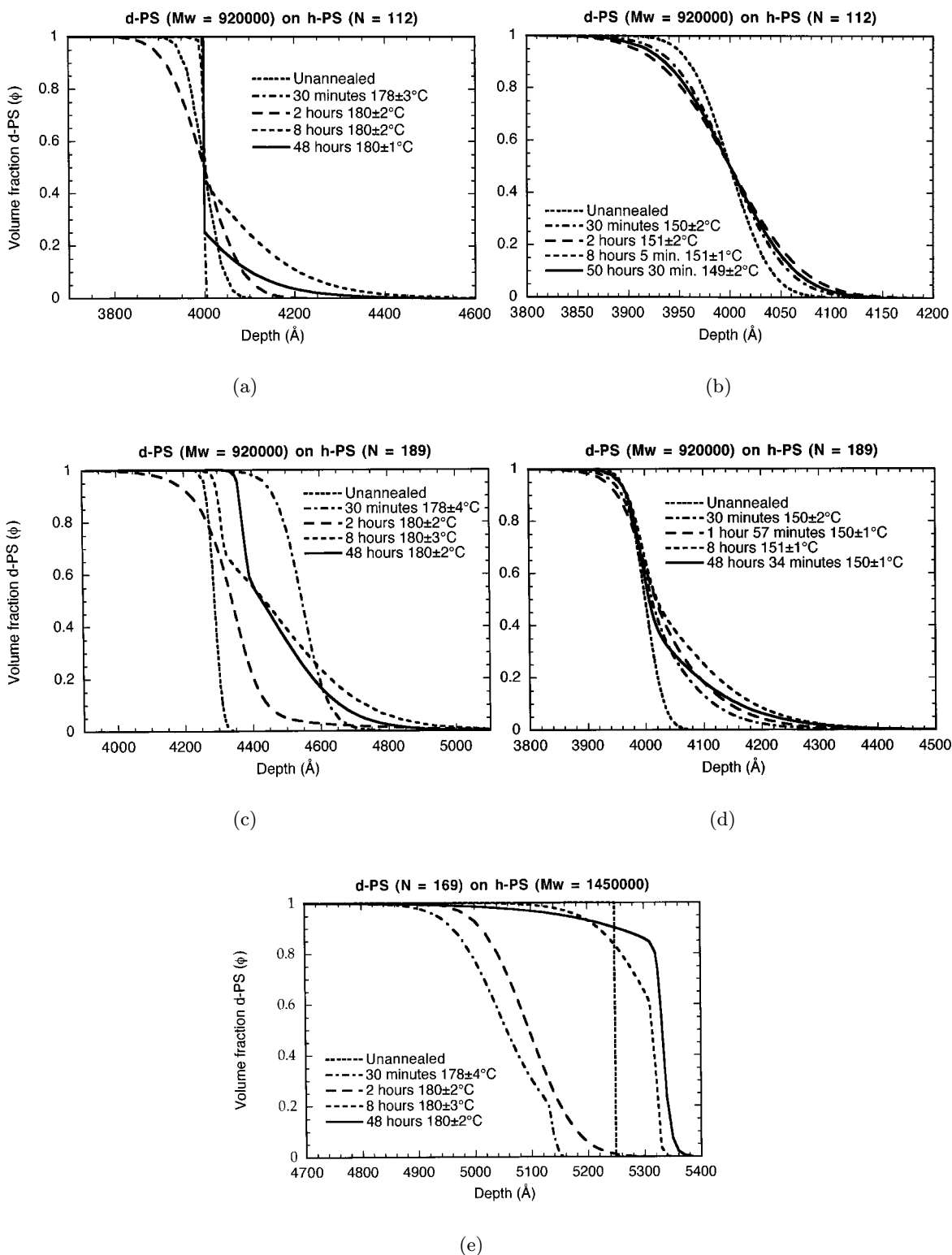
Fig. 5. Volume fraction profiles (obtained using the CRISP reflectometer except where otherwise stated) for the interfaces between linear polymers and polymer networks for d-PS with $Mw = 920\,000$ and h-PS networks with $N = 112$ (a) at 180 °C (the 2 hour data were obtained using EROS) and (b) at 150 °C (all on EROS), $N = 189$ (c) at 180 °C (2 and 48 hours on EROS) and (d) at 150 °C (all on EROS) as well as (e) a d-PS network ($N = 169$) in contact with h-PS ($Mw = 1\,450\,000$) at 180 °C (30 minute and 2 hour data on EROS). The annealing times are approximately 0, 0.5, 2, 8 and 48 hours. In (c) the 2 and 8 hour interfaces (and the unannealed and 8 hour interfaces in (e)) were shifted from the values obtained in the fits to minimise the abscissa scale.

than those cast later (there is also an effect on the viscosity due to evaporation of the solvent but here we believe that the initial concentration of solvent would not have a significant effect on interdiffusion [4]). We note, however, that there are contradictions amongst our experimental results which we attribute to sample preparation. Nevertheless, the amount of data that we have obtained is enough to demonstrate the general trends. These data are shown in Figures 4 and 5.

In this study we limit ourselves to unswollen polymer systems; the swelling that we have mentioned elsewhere in this article takes place only at the interface and the amount of linear polystyrene actually absorbed by the network is negligible. We saw little evidence from our data for absorption of linear polymer by the networks and this is as expected from simple theory. As has been previously pointed out [26,34], the equilibrium swelling of a network occurs when the chemical potential of the surrounding linear polymer and the network are equal, that is when

$$\phi_n^2 \frac{\partial(f_{FH}(\phi_n)/\phi_n)}{\partial \phi_n} = 0, \tag{9}$$

where $\phi_n = 1 - \phi$ is the volume fraction of the network. In all of the systems described below, we calculate much less than 1% linear polymer in the network assuming homogeneous swelling. Other estimates following the work of Bastide *et al.* [34] would lead to even less absorbed linear polymer by the network. This is due to the use of a different form of f_{FH}.

3.2.1 Interfacial profiles (h-PS network with $N = 45$)

One can not easily break the data down into a simple plot of interfacial widths against time as in the preceding section. In order to discuss and highlight the various trends we shall need to discuss each set of data in turn. We commence with a discussion of the volume fraction-depth profiles presented in Figure 4.

d-PS (Mw = 137 000) on h-PS (N = 45)

First of all, we note that the shift in the position of the interface is of the order of ±50 Å, only 1.5% of the thickness of the d-PS layer. We also see that the unannealed interface is surprisingly wide, a trait which is also visible in most of the unannealed samples for the network-network interface study (Sect. 3.1). After 30 minutes annealing, the interface increases in width slightly but remains Gaussian (symmetric) with a width of about 70 Å. The profile after 2 and 8 hours of annealing is similar to that of the 30 minute sample and it is only at 49.5 hours when it becomes asymmetric. It is likely that after this time the d-PS has found its way into the network and has started swelling it at the interface. This is a rather slow process since the self diffusion of the linear polystyrene would be expected to correspond to a diffusion length of more than 1 μm after 2 days annealing at 180 °C [35].

d-PS (Mw = 244 000) on h-PS (N = 45)

When we increase the Mw of the d-PS to 244 000, a noticeable difference in the interfacial profile appears, confirmed when the Mw is increased further to 380 000. On annealing, the interface consists of a combination of a sharp component and a "front" of linear polymer leeching into the network (up to a distance of about 200 Å from the interface). After this the interface broadens gradually with little difference between the 8.5 and 49 hour data. We presume that this indicates a slow relaxation of the network. In particular, we do not see the asymmetric profile after 49 hours that we described for the d-PS with $Mw = 137\,000$. This might be simply because the kinetics is much slower for this larger Mw polymer rather than the possibility that there is no final penetration.

d-PS (Mw = 380 000) on h-PS (N = 45)

We note that the evolution of the interface is the same as for the case of the d-PS of Mw 244 000. In a more detailed observation we should note that the 2 hour profile appears slightly broader than the 8 and 51 hour profiles (but not by any significant amount).

d-PS (Mw = 610 000 and Mw = 920 000) on h-PS (N = 45)

These two sets of profiles are very similar. The interface remains Gaussian with a width of approximately 80 Å in both cases after annealing. There is neither any evidence of any penetration of the network by the linear polymer nor of the sharpening that we see in the 30 minute profiles for the samples with the d-PS Mw's of 244 000 and 380 000. We conclude by suggesting that there is no significant change in these profiles after 2 days annealing at 180 °C.

3.2.2 Discussion of the interfacial profiles (h-PS network with $N = 45$)

We see that only for the case of the polymer with $Mw = 137\,000$ is there any substantial asymmetric interface after two days annealing at 180 °C (the longest time used in our measurements). For the polymers of $Mw = 244\,000$ and 380 000 we see that after 30 minutes annealing there is also an asymmetric interface which we should attribute to different physical origins. The interface is composed of an interface sharper than that of the unannealed sample and a more shallow front. It is not clear why this unexpected result should exist but we speculate that the sharp part of the interfacial profile is due to an improvement in the contact between the two layers after annealing. The "front" component is simply due to interpenetration of the network by the linear polymers.

The higher Mw linear polymers do not show any significant change in volume fraction profile during annealing. This hints that there is an important effect of immiscibility here, with consequences for the free energy of mixing of a polymer network (we see later that, at the interface

of less crosslinked networks, such high Mw polymers are more mobile). This gives us a clue as to the kinetics of the growth of the profile which takes place in these polymers. For polymers with Mw below a certain cut-off value, which for our $N = 45$ network is between 380 000 and 610 000, we have the following stages:

1. The unannealed samples consist of a simple undiffused rough interface. These networks ($N = 45$) were annealed at 180 °C for a short time (between 30 minutes and 2 hours) before the linear polymer film was floated on. This was to ensure that no solvent remained trapped in the network but could also generate a large surface roughness.

2. The early stages of annealing consist of the initial interpenetration of the network by the linear polymer. That the interpenetration of the networks proceeds asymmetrically rather than by the broadening of the interface implies that there is a slow part and a rapid part to this interpenetration. The linear polymer finds it initially relatively easy to cross the boundary with the network (there may be "holes" or other "soft" regions present at the surface of the network). This is how the asymmetric interface is formed in the samples with the d-PS Mw's of 244 000 and 380 000 after 30 minutes annealing. That this was not seen in the sample with $Mw = 137\,000$ is probably testament to the greater mobility of this, the lowest Mw polymer used in the study. (This is plausible since, if the diffusion has a Mw^{-2} behaviour close to a volume fraction of zero [35], the diffusion length of the 137 000 sample would be nearly a factor of two greater than that of the 244 000 sample.)

3. The interface broadens as polymer continues to intrude into the network. The profile becomes more symmetric. This is a surprising result which is difficult to explain definitively. We suggest that the network may be relaxing after having been initially swollen by the linear polymer. We note that the more shallow "fronts" become slightly less visible to neutrons when the network broadens (one now has a contrast between the broad interface and the front which is not as strong as the contrast between a sharp interface and this front).

4. In the case of the $Mw = 137\,000$ polymer the final interface (after two days) is asymmetric. This suggests that the bulk of the network is absorbing a small amount of polymer. We cannot say if this is the case for the other samples because they would need further annealing. Certainly this final swelling process is very slow and the fact that there is no observed development of the profile for the 244 000 and especially the 380 000 Mw samples should not be taken to mean that the sample has equilibrated. There are, after all, no substantial changes to the profile for the $Mw = 137\,000$ (fastest) sample before the 48 hours (longest) annealing time.

In the next section we discuss some problems with sample reproducibility. With the experiments described above we do not have such problems because the same sample was used for each annealing time. If, however, a sample here was in any way unrepresentative, we should not notice this from the growth of the interface. We simply point out here that the data behave reasonably systematically and that there are no obvious "rogue" data sets.

3.2.3 Interfacial profiles (less crosslinked networks)

We have also looked at the highest Mw d-PS sample (920 000) with less crosslinked networks. In these samples the network was not annealed before floating on the linear polymer layer. It is therefore possible that a certain amount of solvent remained trapped in the network, enhancing the diffusion of the linear polymer. It may also be that the crosslinking still had some way to go before the reaction had completed. The profiles are shown in Figures 5a-d. Two crosslinking densities for the d-PS networks have been used, $N = 112$ and 189 and the samples have been annealed at 150 and 180 °C. The data for the samples that were annealed at 150 °C were obtained on EROS, using the unannealed sample from the set at 180 °C. These two unannealed samples were measured on both reflectometers and the same profile resulted.

We also describe profiles for the inverse system, a (relatively) lightly crosslinked d-PS network ($N = 169$) on a h-PS linear polymer film of a large Mw (1 450 000) annealed at 180 °C. These data were obtained on both EROS and CRISP (the data and fits for this system are shown in Fig. 3). The interfacial profile is shown in Figure 5e (for comparison with Figs. 5a-d, one should invert the page).

d-PS (Mw = 920 000) on h-PS (N = 112) (180 °C)

After 30 minutes we see a dramatic sharpening of the interface and no penetration across the boundary. The interfacial width is about 1 Å (although we can increase this by a factor of two or three without having any major effect on the quality of the reflectivity fit). After 2 hours a wider symmetric interface is observed. A subsequent measurement of the same sample after a further 7 hours annealing (9 hours in total at 180 °C) showed that the profile had changed little (a slight increase in the Gaussian width from 66 to 83 Å). We feel compelled to discard this sample from our discussion but note its presence as due to sample creation difficulties. Returning to the series, we see that after 8 hours there is significant build up of a linear polymer front swelling the network. This has diminished after 48 hours, a surprising result and one that would be tempting to blame on sample preparation were it not repeated below. We note that the sharp contribution to the interface in the 30 minute, 8 and 48 hour samples always remains less than 10 Å.

d-PS (Mw = 920 000) on h-PS (N = 112) (150 °C)

For these experiments the unannealed sample of the above was further annealed and more data obtained on EROS. The results are very similar to the 2 hour sample described in the last paragraph. The interfacial width remains at about 70 Å which completely contradicts the results at

180 °C and the other results described below. We postulate that the network in this case (and in the above 2 hour sample at 180 °C) was spin cast from a solution that had become very viscous and that the network was beginning to form before spin casting. We have no further evidence to back this up as we do not know in what order these networks were spin cast (although we equally cannot deny the possibility of the converse where these networks were formed from the "fresh" solution and the other samples from a solution in which crosslinking had begun before spin casting).

d-PS (Mw = 920 000) on h-PS (N = 189) (180 °C)

Here we see the interface broaden slowly after 30 minutes and then 2 hours annealing. After 2 hours we note the appearance of a small front penetrating over 500 Å across the interface. This was repeatedly verified by refitting the data to see its significance on χ^2. The effect is real (the fit has a χ^2 of 2.8, about 0.4 smaller than the best equivalent symmetric profile, demonstrating the sensitivity of NR) and because it was not observed in other data should not be taken as evidence that it is not present; the simplex fitting method may simply have more difficulty in finding the minimum. After 8 hours we have a build up of linear polymer swelling the interface and this is also true of the 48 hour data (although, in the case of the 48 hour data, the quantity has diminished slightly, similarly to the d-PS diffusing into the network with $N = 112$ at 180 °C). In both cases the sharp part of the interface has a width of 11 Å.

d-PS (Mw = 920 000) on h-PS (N = 189) (150 °C)

Again, the unannealed sample of the last set of experiments was used and annealed at four annealing times and experiments on this sample performed on EROS. Here we see a gradual build up of linear polymer swelling the network for 30 minutes, 2 and 8 hours. Again, after 48 hours the quantity of the d-PS diminishes.

d-PS (N = 169) on h-PS (Mw = 1 450 000) (180 °C)

The complementary experiment, in which the network is deuterated, reinforces the results discussed above. After 30 minutes one sees an asymmetric profile in which the linear h-PS has begun to cross the boundary and to swell the d-PS network. After 2 hours the profile is symmetric again (a width of 93 Å) although, in truth, not that much different from the 30 minute data. After 8 hours the volume fraction of h-PS swelling the network has decreased although the depth that it penetrates has increased. This effect further continues after 48 hours. We note that again, in the 8 and 48 hour samples, the interface remains sharp (less than 10 Å).

3.2.4 Discussion of the interfacial profiles (less crosslinked networks)

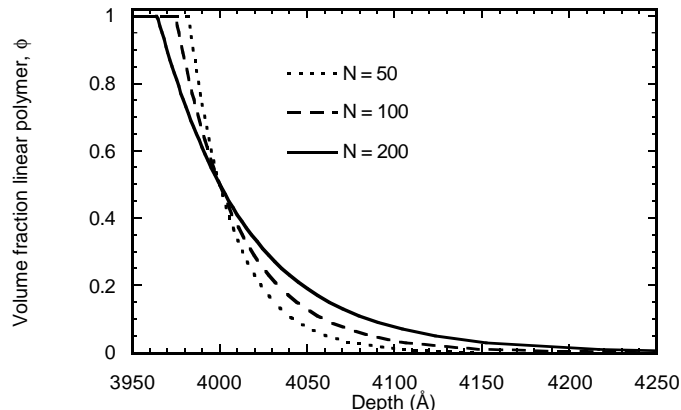In summary, the general trend shows interfaces consisting of two parts. We have a relatively sharp component

Fig. 6. Theoretical equilibrium volume fraction profiles for a d-PS linear polymer ($Mw = 920\,000$) diffusing into h-PS networks with $N = 50$, 100 and 200. The interface has been set at a depth of 4000 Å.

(10 Å or less) and a more shallow component which eventually decreases with increasing annealing time. Both of these phenomena are very surprising. The fact that we usually see more interpenetration for the 8 hour sample than that of 48 hours implies that the linear polymer is leeching into the bulk of the network rather slowly. We conclude that the polymer has found its way into "soft" regions present at the surface. This swells the network which relaxes by expelling the polymer into the bulk of the network. That this was not visible for the d-PS of Mw 610 000 and 920 000 in contact with $N = 45$ implies that there may be a correlation with the size of these "soft" regions and the crosslinking density. Smaller "soft" regions of the $N = 45$ network make it harder for higher Mw linear polymers to enter [10,34].

We now consider the temperature dependence of the evolution of these profiles. If we attribute the measurements at 150 °C for the d-PS ($Mw = 920\,000$) sample diffusing into the h-PS network ($N = 112$) as being to a sample "different" in some way to most of the others, we are only left with the diffusion into the $N = 189$ h-PS network as an example with which we can draw any conclusions about temperature dependence (Figs. 5c and d). The asymmetry is immediately obvious in the 150 °C measurements (Fig. 5d) but in both cases we see a decrease in the quantity of d-PS across the interface only after 48 hours. This implies that there is not much temperature dependence in the relaxation of the network. For comparison with linear polymer dynamics we note that the (reptation) self diffusion coefficient for polystyrene at 180 °C is 28 times larger than at 150 °C [35] (corresponding to a respective 28 and just over five-fold increase in the diffusion time and length at 180 °C from 150 °C).

Again, we can calculate a crude theoretical equilibrium profile using the theory of Broseta *et al.* [3]. In order to do this we need to solve equation (3) for the case where one component is a network and the other is a linear polymer.

This equation (10) must be solved numerically [31];

$$\frac{\chi \left(w\frac{\partial \phi}{\partial z}\right)^2}{4\phi(1-\phi)} = \frac{\phi}{N_A}\ln \phi + \chi\phi(1-\phi)$$
$$+ \frac{1-\phi}{2N}\left(\frac{1}{(1-\phi)^2} - 1 + \ln(1-\phi)\right) \quad (10)$$

where N_A is the chain length of the linear polystyrene.

Numerical solutions are shown in Figure 6 for networks of $N = 50$, 100 and 200 at 180 °C. We note that the profiles are not of the same shape as those obtained in our data but that the same depth penetration (of the order of 200 Å) of the linear polymer into a network ($N = 100$ or 200) as we have seen in our data is predicted by the theory. We can explain this by remembering that we actually have two contributions to the interface. If we remove regions whereby the linear polymer cannot diffuse into the network (due to a high crosslinking density, for example) then we should have only regions where this front appears and its height would have to be multiplied accordingly. (We assume the neutron coherence length to be large enough to average over these regions.) We also note that we cannot say if our samples are close to equilibrium. We have shown neither temperature nor molecular weight dependence in this figure as this does not appear to be significant. The theoretical profile is controlled by the size of the network. For example, the $Mw = 920\ 000$ d-PS diffusing into the network $N = 100$ has the same profile at both 180 °C and 150 °C. Similarly, there is very little difference between the $Mw = 920\ 000$ d-PS diffusing into the network $N = 50$ and the $Mw = 137\ 000$ d-PS diffusing into the same network (this can be seen from Eq. (10)). We note that the above takes no account of the distribution in N, and nor are "dangling ends" catered for. For the most part, dangling ends can be dismissed because the size of the interface is considerably larger than the expected size of the dangling ends. The polydispersity of N is more significant. The original paper by Broseta *et al.* [3] extended the theory to include polydispersity but their work considered the interface between asymmetric linear polymers (they found that the interfacial tension was lowered because, in polydisperse systems, smaller polymers tended to aggregate at the interface). One could not really make the same extension here because the network is not mobile in the same way as linear polymers are.

4 Summary and conclusions

We have shown that the interface between two polymer networks broadens to a degree that can only be understood if one accepts the movement of more heterogeneous regions. This interfacial width might contain regions of network which are "knotted". If this is so then there could be a considerable contribution to the adhesion between these networks. This means that the two networks may well be stronger than two equivalent linear polymers, where entanglements only concern single chains in comparison with the networks where entanglements would

concern much larger regions. There is a small variation with crosslinking density as expected, although this is hard to quantify. The kinetics of the interfacial broadening is rather rapid, having reached completion with the interface not changing in size after two hours annealing at either 150 or 180 °C.

The situation for a linear polymer and a network is much more complicated. The kinetics appears to progress in a fashion rather difficult to follow. This has been further hindered by problems of reproducibility. Nevertheless, the important physical behaviour at the linear polymer-network interface can be summarised in four parts depending on the Mw or the value of N. We call low Mw when $Mw < 500\ 000$ and small N when $N < 100$. The rest we consider "high" or "large":

1. Low Mw-small N: Initially a small amount of linear polymer enters the network which then relaxes forming a symmetric (error function) profile of a relatively narrow width (typically around $\sigma = 70$ Å in our work).
2. High Mw-small N: No noticeable change in the shape of the profile over the time scales studied.
3. Low Mw-large N: The linear polymer rapidly diffuses into the network. This is discussed elsewhere [4].
4. High Mw-large N: Very asymmetric profiles are observed. The amount of visible interdiffusion (the diffusion front) actually decreases with time, presumably because the linear polymer has been able to eventually diffuse into the bulk of the network. Aside from this front, the original network polymer interface remains and is still quite pronounced (< 10 Å) even after 48 hours annealing.

We have calculated the theoretical equilibrium profile for the interface between a linear polymer and a network and this differs from our results in that a molecular weight dependence is not observed in the theory. The theoretical calculation predicts a temperature independent profile which is similar in shape to the diffusion front that we see in our results but which does not take account of the original interface. The theory that we have used takes no account of the polydispersity in N.

The results that we have presented for network-network and network-linear polymer interfaces can only be considered a first step. The reproducibility of the samples is difficult and our conclusions can only be considered as qualitative rather than quantitative. We cannot say how much our results are influenced by the crosslinking method employed but we again note that every crosslinking method will somehow perturb the network.

These results could be complemented by some measure of the interfacial strength. We consider two mechanisms for the build up of the interfacial profiles, one whereby the linear polymer fills "holes" (imperfections in the network close to the interface) and the other whereby the linear polymer actually swells "soft" regions of the network. In the former case the interfacial strength will be much weaker than in the latter case. Similarly, a bumpy network-network interface with little interpenetration of the polymers would be considerably weaker than that of

an interface in which the networks do physically interpenetrate. Indeed, the possibility of large movements of soft regions to cause an increase in the interfacial strength in comparison to that with two linear polymers needs to be explored. Such experiments are in progress.

References

1. H.H. Kausch, M. Tirrell, Ann. Rev. Mat. Sci. **19**, 341 (1989).
2. E. Helfand, Y. Tagami, J. Chem. Phys. **56**, 3592 (1972).
3. D. Broseta, G.H. Fredrickson, E. Helfand, L. Leibler, Macromolecules **23**, 132 (1990).
4. M. Geoghegan, F. Boué, F. Abel, in preparation.
5. X. Zheng, M.H. Rafailovich, J. Sokolov, X. Zhao, R.M. Briber, S.A. Schwarz, Macromolecules **26**, 6431 (1993).
6. W. Wu, W.E. Wallace, J.H. van Zanten, B.J. Bauer, D. Liu, A. Wong, Polymer **38**, 2583 (1997).
7. M. Antonietti, H. Sillescu, Macromolecules **18**, 1162 (1985).
8. C. Marzolin, Thesis, Université de Pierre et Marie Curie, Paris, 1995.
9. F. Brochard-Wyart, P.-G. de Gennes, L. Léger, Y. Marciano, E. Raphaël, J. Phys. Chem. **98**, 9405 (1994).
10. F. Zielinski, Thesis, Université de Pierre et Marie Curie, Paris (1991).
11. F. Zielinski, M. Buzier, C. Lartigue, J. Bastide, F. Boué, Prog. Coll. Polym. Sci. **90**, 115 (1992).
12. A. Ramzi, F. Zielinski, J. Bastide, F. Boué, Macromolecules **28**, 3570 (1995).
13. E. Mendes Jr., P. Lindner, M. Buzier, F., Boué, J. Bastide, Phys. Rev. Lett. **66**, 1595 (1991).
14. E. Geissler, F. Horkay, A.-M. Hecht, M. Zrinyi, Phys. Rev. Lett. **71**, 645 (1993).
15. J. Penfold, R.K. Thomas, J. Phys. Condens. Matter **2**, 258 (1990).
16. T.P. Russell, Mater. Sci. Rep. **5**, 171 (1990).
17. R.A.L. Jones, L.J. Norton, K.R. Shull, E.J. Kramer, G.P. Felcher, A. Karim, L.J. Fetters, Macromolecules **25**, 2359 (1992).
18. M. Geoghegan, R.A.L. Jones, D.S. Sivia, J. Penfold, A.S. Clough, Phys. Rev. E **53**, 825 (1996).
19. K. Kunz, J. Reiter, A. Götzelmann, M. Stamm, Macromolecules **26**, 4316 (1993).
20. S.K. Sinha, E.B. Sirota, S. Garott, H.B. Stanley, Phys. Rev. B **38**, 2297 (1988). Other references can be found in the review by Penfold and Thomas [15].
21. The NR profiles were fitted using a Power Macintosh 7200 computer and took up to 20 minutes per fit. The simplex is not the most efficient of routines (*Numerical Recipes in C: The Art of Scientific Computing 2nd ed.*, W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery (Cambridge University Press, Cambridge, 1992)) and this was compounded by the most complicated profiles being divided up into 50 steps and the Gaussian smoothing routine used in the fit was itself split up into up to 35 steps.
22. R.A.L. Jones, in *Polymer Surfaces and Interfaces II*, edited by W.J. Feast, H.S. Monro, R.W. Richards (Wiley, Chichester, 1993), p. 71.
23. J.D. Ferry, *Viscoelastic Properties of Polymers 3rd ed.* (Wiley, New York, 1980).
24. J. Lal, J. Bastide, R. Bansil, F. Boué, Macromolecules **26**, 6092 (1993).
25. If an arbitrary surface is created by slicing through a polydisperse polymer solution, the number of times a chain crosses the interface scales as $\sqrt{n}$, where n is the chain length. Thus longer chains are preferentially adsorbed at the interface in the absence of enthalpic interactions.
26. F. Brochard, J. Phys. France **42**, 505 (1981).
27. P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
28. G.H. Fredrickson, in *Physics of Polymer Surfaces and Interfaces*, edited by I.C. Sanchez (Butterworth-Heinemann, Boston, 1992), p. 1.
29. F.S. Bates, G.D. Wignall, Macromolecules **19**, (1986) 932.
30. The formula for the interfacial width is derived from a hyperbolic tangent profile. Our experimental widths are for a complementary error function profile. The hyperbolic tangent width remains at about 90% that of the error function.
31. This equation should, in principle, be equal to the minimisation of the Euler equation in Cahn's theory of wetting (J.W. Cahn, J. Chem. Phys. **66**, 3667 (1977)) in the strong segregation limit of the random phase approximation [28]. It is a factor of four out and in order to make the results agree with this theory it is necessary to contract the interface by a factor of two. This means that interfacial widths are halved.
32. P.J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953), p. 578.
33. J.-U. Sommer, T.A. Vilgis, G. Heinrich, J. Chem. Phys. **100**, 9181 (1994).
34. J. Bastide, S. Candau, L. Leibler, Macromolecules **14**, 719 (1980).
35. The intradiffusion for this polymer has been measured elsewhere at 150 °C [4] and we can scale the result to 180 °C by using the data of P.F. Green, B.L. Doyle, Macromolecules **20**, 2471 (1986). The interpenetration is described by interdiffusion which has a complex Mw dependence. However, at small volume fractions the Mw dependence of the diffusion coefficient is expected to be similar to that of the intradiffusion coefficient.