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The kinetics of polymer brush penetration in to a high molecular weight matrix

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Neutron reflectivity has been used to measure concentration profiles of polymer brushes as they penetrate a high molecular weight polymer matrix. The brushes consist of end-functionalized deuterated polystyrene strongly grafted to a silicon substrate, in a melt matrix of (protonated) polystyrene. Initially the brush is totally excluded from the matrix. The rate at which the brush chains penetrate the matrix was investigated by measuring the brush segment density profiles after annealing the samples above the glass transition temperature for a range of times. We find that when the initial interface between the brush and the matrix is sharp, there is at first a rapid penetration of the brush into the matrix. This is followed by a slow approach to equilibrium, which is not achieved after annealing for a day. These observations are consistent with the predictions of a recent analytical theory and computer simulations. In contrast, samples with an initially diffuse interface reach equilibrium quickly. Two different matrix polymers were used to investigate the effect of the matrix molecular weight. Comparison has been made with a mean field model for the equilibrium brush profile. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

In many composite and multi-phase materials, the properties of the material are dominated by the properties of the interfaces between phases since interfaces are usually the sites most susceptible to deformation or fracture. One interfacial system which has been the subject of many studies[1], both experimental[2–6] and theoretical[7–9], over the last decade consists of polymer layers which are attached by one end to a surface. These systems (known as brushes) are of considerable importance because of their potential applications in composite materials, adhesives, lubricants and colloidal stabilizers amongst others. Typically the brush is formed from a diblock copolymer adsorbed to the interface between two homopolymer layers or by a layer of polymers which are grafted by a functional group which exhibits an affinity for the surface.

There has been a substantial amount of experimental work, driven by technological applications, on measuring the fracture toughness of polymer interfaces which have been reinforced by brushes[10,11]. Polymers grafted at the interface between a polymer and a non-polymeric substrate increase the bonding of the two materials. The interfacial strength depends upon the extent of the penetration of the brush polymer in the bulk, and is usually due to entanglements between the brush and the bulk polymer. As a crack propagates along the interface the grafted chains either pull out or break. An important corollary of this work is the study of the healing of such interfaces after fracture. Healing can take place by a process in which chains that have been pulled out penetrate back into the bulk polymer. Recently, this healing process has been investigated theoretically by O'Connor and McLeish[12] (hereafter referred to as O & M). Computer simulations have been produced by Deutsch and Yoon[13]. Here we report an experimental study of this process.

EXPERIMENTAL

Monodispersed carboxy-terminated deuterated polystyrene, dPS(COOH), was obtained from Polymer Laboratories. It was modified by a method previously developed for converting a carboxylic acid end group into a tri-ethoxy silane group[2], which is known to bond strongly to silanol group in a layer of silicon oxide[14]. Single crystal silicon wafers (5 cm diameter) were cleaned with toluene and methanol. The native oxide was stripped by placing the wafers in a bath of hydrofluoric acid. The wafers were then etched in oxygen plasma for 3 min to grow a uniform surface layer of silicon oxide 20–25 Å thick. The oxide layer was characterized by ellipsometry. The tri-ethoxy silane terminated polymer was spin coated from toluene solution onto the wafers to produce a polymer layer ~ 300 Å thick. The coated wafers were annealed for 24 h in a vacuum oven at 184°C to enable the end groups to move to and graft to the substrate. The polymer that had not grafted was removed by washing the surface with toluene several times. The thickness of the layer was measured by ellipsometry after each wash. A layer thickness of ~ 90 Å was reached after a few washes. The thickness did not decrease below this value on further washing.

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Thus the remaining polymer is strongly grafted to the silicon wafer.

The polymer matrix layers were produced in two ways. In the first method the layers were made by spin coating a solution of protonated polystyrene (hPS) onto a 6 cm square glass slide to form films ~ 2500 Å thick. These films were carefully floated off the glass in a bath of distilled water and then picked up on the silicon wafers onto which the brush had previously been grafted. The samples were left to dry in a desiccator for several hours in order to remove water trapped between the brush and the matrix layer.

In the second method, samples were also made by spin coating the matrix layer directly onto the brush. In this case the initial conformation is not a sharp interface between the brush and the matrix as for the floated samples but a much broader one since substantial mixing can take place due to the presence of the solvent during the second spin coating. It has previously been shown that this procedure produces brushes which reach their equilibrium conformation fairly quickly[2].

The samples produced by the first method were annealed in a vacuum oven at 150°C for a range of times from 15 min to 23 h. The samples produced by the second method were annealed for 23 h. It is difficult to anneal samples reliably for times shorter than about 15 min for two reasons: firstly it takes a few minutes for the sample to equilibrate in vacuum since heat transfer to the polymer takes place by conduction through the silicon wafer; secondly, temperature fluctuations arise when the oven door is opened. Two different molecular weight matrix polymers were used. A very high molecular weight (8×10^6) was chosen in order that the matrix should resemble a network. The reptation time of the 8 M hPS at 150°C is approximately 17 days, i.e. much longer than the longest experimental annealing time. A lower molecular weight matrix polymer, 500.8 k ($\tau_{\mathrm{rep}} \sim 5$ min) was also used to provide a comparison. The detailed characteristics of the polymers are given in *Table 1*.

Neutron reflectivity experiments were performed on these samples. This technique is a powerful experimental tool which can provide detailed segment density profiles of polymers near surfaces[2,3,6]. The technique has been described in detail elsewhere[6,15]. The reflectivity data were taken at room temperature on the CRISP time-of-flight reflectometer at the ISIS facility, Rutherford Appleton Laboratory. The data were analysed by producing fits from model profiles. These were refined to minimize the χ^2 parameter by a simplex fitting routine and also by using maximum entropy methods[16]. The two different analysis methods gave very similar results. The prior knowledge that the deuterated layer was fixed at the substrate removes some of the ambiguities that can arise in the analysis of reflectivity data (because the data cannot be directly inverted to give a scattering length density profile). We can, therefore, be confident that the profiles derived from the reflectivity data closely represent the segment density profiles of the samples.

Table 1 Characteristics of the polymers used in this study (all obtained from Polymer Laboratories)

Polymer	Abbreviation	M_w	M_w/M_n
End-functionalized deuterated polystyrene	dPS	79 750	1.04
Protonated polystyrene	hPS (500 k)	500 800	1.06
Protonated polystyrene	hPS (8 M)	8 000 000	< 1.07

RESULTS

Figures 1 and *2* show reflectivity data, together with the best fits, for the 8 M and 500 k hPS matrices. In both cases the reflectivity changes substantially on annealing for 15 min, demonstrating that the conformation of the brush chains has changed significantly. However, thereafter there is little change on further annealing. The reflectivity near the critical edge is particularly sensitive to changes in the brush profile because neutrons with wavevector (k) close to the critical value can tunnel through the potential barrier at the substrate which arises from the high scattering length density deuterated polymer in the brush. Tunneling is a very sensitive function of the barrier height

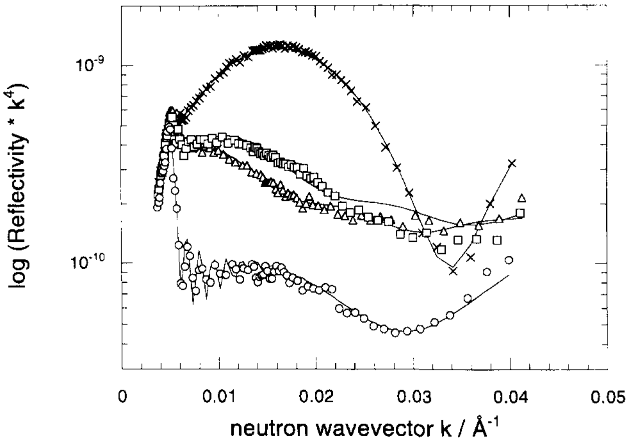

Figure 1 Neutron reflectivity data (plotted as reflectivity × k^4) for the 8 M hPS matrix: unannealed samples (crosses), 15 min anneal (triangles), 23 h (squares) and the spin coated matrix (circles). The reflectivity curves from the 1 and 4 h samples are not shown as they are almost identical to the 23 h one. The solid lines are best fits from which the profiles in *Figure 3* are derived

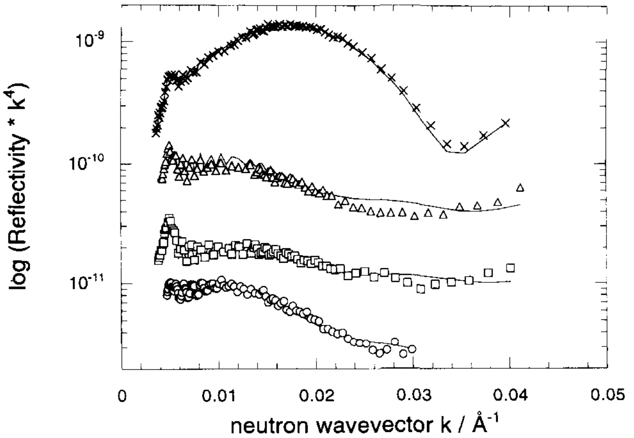

Figure 2 Neutron reflectivity data (plotted as reflectivity × k^4) for the 500 k hPS matrix: unannealed samples (crosses), 15 min anneal (triangles), 23 h (squares) and the spin coated matrix (circles). The reflectivity curves from the 1 and 4 h samples are not shown as they are almost identical to the 23 h one. The data have been vertically shifted for clarity. The solid lines are best fits from which the profiles in *Figure 4* are derived

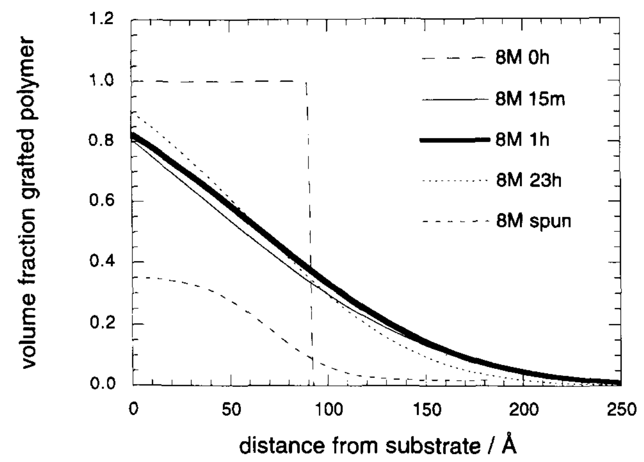

Figure 3 Brush profiles for the 8 M hPS matrix

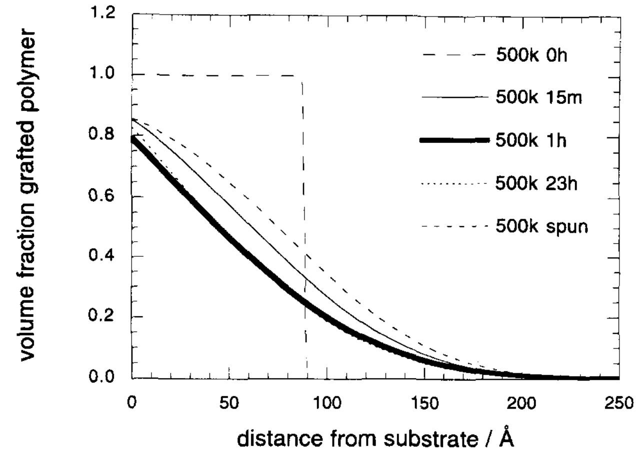

Figure 4 Brush profiles for the 500 k hPS matrix

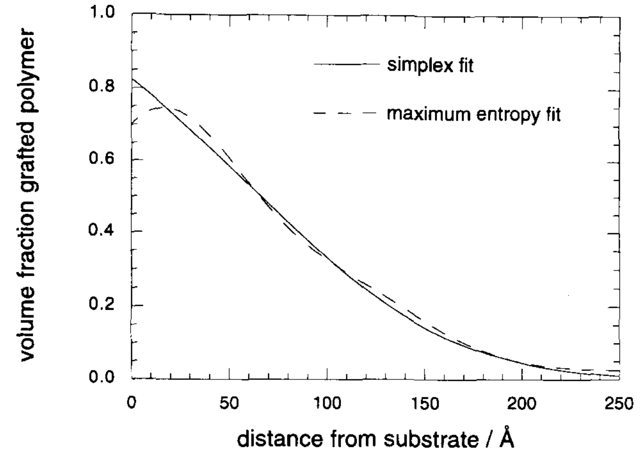

Figure 5 Brush profiles (8 M matrix, 1 h anneal) from two different fitting processes: simplex error function (solid line) and maximum entropy freeform profile (dashed line)

and thickness, so very small changes in the profile can have a substantial effect on the reflectivity.

Brush profiles (derived from the fits shown in *Figures 1* and *2*) for the 8 M and 500 k molecular weight matrices are shown in *Figures 3* and *4*, respectively. The fits have normalized values of χ^2 in the range 2–6. These fits were obtained using an error function profile for the brush with the simplex minimization routine. *Figure 5* shows the comparison of the simplex and maximum entropy profiles for a typical sample. The two different fitting methods produce profiles which are in very close agreement. The maximum near the substrate arises from the maximum entropy method which penalizes sharp gradients in the profile. A similar maximum can be included in the error function profile, but this modification reduces the quality of the fit. The close agreement gives us confidence that the profiles are correct.

When interpreting the results of neutron reflectivity experiments to study interfaces, it is important to consider the contribution of capillary wave fluctuations at the interface. These represent a spatial variation in the position of the centre of the interface and are averaged by neutron reflectivity experiments. They have been shown to produce a significant contribution to the apparent interface width between immiscible homopolymer[17]. However, the contribution to the interface width due to fluctuations is much smaller for brushes. This is because the fluctuations are suppressed when one of the chain ends is tethered to a flat surface. Fredrickson *et al.*[18] have calculated the modes which will contribute to the fluctuations by assuming that all ends of the brush chains lie at the interface. Calculations for a neutral matrix indicate that the root mean square amplitude of the fluctuations is ~ 2 Å (Turner, M. S., personal communication), so they will produce only a very small increase in the experimental interfacial width. Therefore, in these experiments we can neglect them.

The interface between the brush and the matrix in the unannealed sample is very sharp (the width is 2 Å). On annealing there is a rapid and substantial change in the profile. The sharp interface between the grafted layer and the matrix becomes much broader (≈ 200 Å). In the 8 M matrix there are no further changes on annealing for up to 23 h. In the 500 k matrix, there is a small change between 15 min and 1 h, and then no further change up to 23 h. There is a change in the total adsorbed amount (approximately a 10% reduction) between the unannealed sample and the annealed ones. This must be due to some of the brush polymer desorbing from the substrate, so that the brush chains are in equilibrium (i.e. have the same chemical potential) with the desorbed chains in the bulk. Nuclear reaction analysis experiments indicate that the amount of end-functionalized chains in the matrix is very small ($< 0.5\%$). In any case this should not affect the behaviour of the grafted chains.

We do not believe that this is the equilibrium brush conformation because samples in which the matrix was spin coated onto the grafted layer show a different profile. For the 8 M matrix, a substantially smaller grafting density was accidentally used. In this case we can make no direct comparison between the 23 h sample (23 h) and the spin coated one (sc). However, it is apparent that the shape of the sc profile is very different from the 23 h one. In particular the sc profile is flat near the substrate, whereas for the 23 h sample the brush volume fraction decreases rapidly in this region. A similar observation can be made for the 500 k matrix, where the grafting density used was much closer to that of the other samples. This allows a direct comparison of the profiles. Again the sc brush volume fraction decreases slowly near the substrate whereas the 23 h one drops off more rapidly, the 23 h profile is concave whereas the sc one is convex. The convex shape appears to be characteristic of equilibrium brush profiles in a neutral matrix[2,6].

COMPARISON WITH MEAN FIELD THEORY

We can be confident that the sc sample profile is the equilibrium one because we can compare it to a profile obtained from self-consistent mean field theory (SCMF). SCMF theory relies on the mean field approach[19], where the influence of the many chains interacting with a given chain is represented by a spatially varying mean field. The conformation of the test chain is found from an initial guessed chemical potential. The chemical potential distribution is then recalculated from the test chain conformation, and the process repeated until a self-consistent solution is reached. Numerical solutions of the SCMF equations on a lattice for grafted polymer layers have been reported[9]. We have used this method to predict the equilibrium brush profile for these experiments. In the SCMF calculations there is one adjustable parameter. This is the sticking energy of the functional group to the substrate. In this case the actual value of the sticking energy has no significance since it is only used to reproduce the experimental grafting density, which is fixed by the grafting process.

The experimental profiles for the sc and 23 h samples are shown in *Figure 6* for the 500 k matrix, together with the profile derived from SCMF theory (for the same grafting density as the sample). There is fairly close agreement between the sc and SCMF profiles which are different from the 23 h sample. For the 8 M matrix, the high molecular weight necessitates the use of a very coarse lattice in the calculation. There are only a few lattice layers in the brush and it becomes questionable whether the SCMF profile is valid. However, it is well established both experimentally[2,4] and theoretically[9,20] that in a neutral matrix the brush conformation depends only on the matrix molecular weight only when $N_{\mathrm{matrix}} < N_{\mathrm{brush}}$ (N is the degree of polymerization). When $N_{\mathrm{matrix}} = N_{\mathrm{brush}}$, a limiting 'dry brush' regime is reached for which further increases in the matrix molecular weight do not affect the profile. It is, therefore, reasonable to assume that the equilibrium profile for the 8 M matrix, with the appropriate grafting density, will be similar to the 500 k sc sample.

It is important to consider the effects introduced by the difference between protonated and deuterated polymers. It is known that isotopic blends of polystyrene have a non-zero Flory-Huggins interaction parameter (χ)[21,22]. To account for this, a χ of 1.8×10^{-4} is included in the mean field theory. The question of a surface energy difference between deuterated and protonated segments is more complex. Preferential segregation to a free surface in an isotopic blend has been extensively studied in recent years and is well understood in terms of mean field theory[23,24]. The issue of preferential segregation to a silicon oxide surface is less clear. Segregation of the deuterated[25] and protonated species[26], and neither (Geoghegan, M. A., personal communication) have been observed in different studies. A simple enthalpic surface energy difference only accounts well for the segregation in symmetric blends[25], whilst entropic effects dominate in highly asymmetric blends[26]. Previous experiments[2,3,6] have shown that the SCMF theory closely matches the equilibrium brush profile both in a range of molecular weight matrices, and when the brush has been produced by different methods, without including a surface energy difference between the deuterated and protonated segments. We, therefore, consider that comparison of the SCMF profile with the experimental ones is valid. Since there is fairly close agreement between the sc and SCMF profiles, which are different from the 23 h sample in *Figure 6*, it seems likely that the sc profile is the equilibrium one.

DISCUSSION

We summarize briefly the predictions of O'Connor and McLeish[12], together with the results of simulations by Deutsch and Yoon[13] and the experiments of Reichert and Brown[11]. In these studies, the matrix was a permanently cross-linked network. O & M considered the low coverage regime, i.e. when

$$\sigma \ll \frac{1}{b^2 N} \tag{1}$$

where σ is the grafting density and b is the Kuhn length. The grafted chains all lie in a layer at the substrate and are squashed normal to it. O & M predict two important stages in the penetration into the matrix: there is a rapid partial penetration of the bulk, followed by a much slower relaxation to the equilibrium conformation.

Initially the grafted chains all lie in an unentangled layer at the substrate, with the free ends a certain

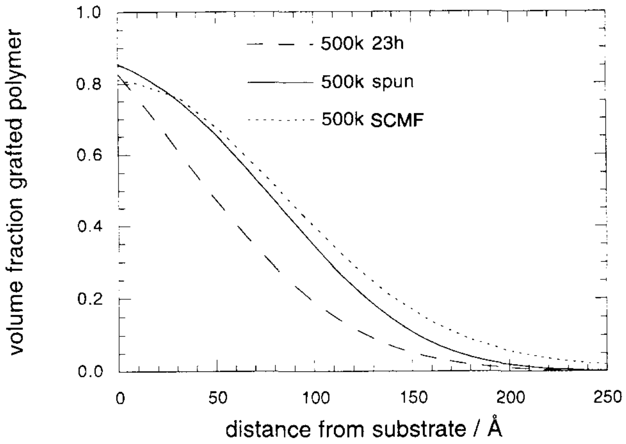

Figure 6 Brush profiles for the 23 h sample (dashed line) and the spin coated sample (solid line) for the 500 k hPS matrix compared with the predicted equilibrium profile (for the same grafting density) from SCMF theory

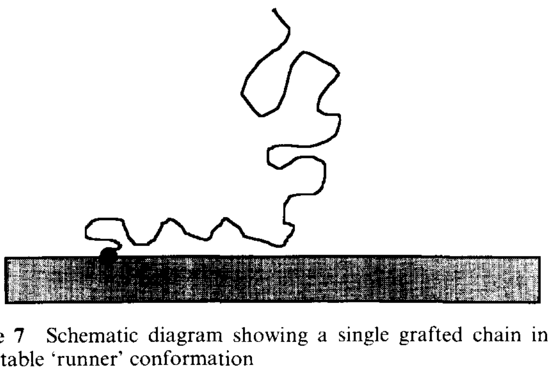

Figure 7 Schematic diagram showing a single grafted chain in the metastable 'runner' conformation

distance away from the grafted end. When the sample is raised above the glass transition temperature, the free end can reduce its entropy by penetrating the matrix. However most of the free chain ends will enter the matrix some distance away from the grafting point, so that a length of the chain remains on the substrate while the rest enters the network. O & M have shown that a metastable equilibrium can be reached with the chains having a temporary fixed length on the substrate and a dangling section in the entangled matrix. They refer to this state as a 'runner' by analogy with plants having trailing surface roots (see *Figure 7*). The penetration of the free ends into the matrix is governed by Rouse dynamics[27] and the characteristic time for the process is given by

$$\tau \approx \tau_1 \left(\frac{a}{2b}\right)^4 \tag{2}$$

where a is the distance between entanglements and τ_1 is the relaxation time of a Kuhn segment. Above the glass transition temperature this time is very short, typically < 1 s.

Once the free chain end is embedded in the matrix, in order to approach its equilibrium conformation (in which the distance between the grafting point and the point where the free end enters the matrix is zero) it has to retract its path in its original tube and tunnel out into a new tube closer to its grafting point. This process is similar to the 'breathing' mode relaxation of star polymers. The time scale for this process is given by the characteristic occupation time of a particular tube. The relaxation time of a star polymer in an entangled melt is given by

$$\tau \sim \exp\left(0.6\frac{N}{N_e}\right) \tag{3}$$

where N_e is the number of segments between entanglements[28]. It is known experimentally that these time scales are long (several days or more) so the approach to equilibrium will be slow. An estimate for the relaxation time of the second stage is [13]

$$\tau \sim \tau_1 N^2 \exp\left[\beta\left(\frac{b}{2a}\right)^{2N}\right] \tag{4}$$

(β is a numerical constant of order 1). This is much longer than the characteristic time for the first stage because of the exponential term.

The simulations of Deutsch and Yoon are in good agreement with O & M. They find the rapid initial penetration. The approach to equilibrium is very slow. Reichert and Brown had a grafting density somewhat higher than that considered by O & M. Their measurements showed a rapid partial recovery of the equilibrium toughness. They found an almost instantaneous rise in the fracture energy to a value considerably greater than that for a sample with no tethered chains at the interface, implying that there is a rapid partial penetration of the network. The fracture energy continued to increase slowly over a period of days, corresponding to the second stage.

Our experiments have a grafting density which is smaller, but not very much smaller, than $1/b^2N$, so we expect the theory of O & M to be applicable. However, they considered a permanently cross-linked matrix rather than a highly entangled melt. The expression for the relaxation time of a star polymer in a network is similar to that in a melt (equation (4)), but with a larger numerical coefficient in the exponential so that relaxation is slower. Therefore, we might still expect to see a two-stage process in the experiments. The second stage will be slow, but not as slow as it would be in a permanently cross-linked matrix.

In our experiments (*Figures 3*, *4* and *6*) there is a rapid initial change which takes place in less than 15 min. Then there is little change as the samples are annealed for up to 23 h. The brush appears to be in the metastable state. We believe that the spin coated sample has the equilibrium profile, which would be reached eventually if one of the other samples were annealed for a sufficiently long time. Our results therefore are consistent with Reichert and Brown's experiments, and the theory and simulations, without however providing a definitive test.

We must also consider the effect of the substrate on the observed kinetics. It has been recently observed that the diffusion coefficient of PS chains very near a silicon oxide surface is about two orders of magnitude less than its bulk value[29]. A preferential attraction of the deuterated monomers for the substrate could also slow down their diffusion. The characteristic diffusion time (the time to diffuse a radius of gyration) of dPS chains in a high molecular weight hPS matrix at 150°C is about 5 s[3], i.e. less than the shortest annealing time in these experiments, even allowing for a substantial reduction in the diffusion coefficient due to the surface. It is clear that since the 15 min and 23 h profiles are almost identical, these experiments are not sensitive to the relatively fine features of the kinetics and only coarse features, such as the metastable state are observed.

A better test of O & M's theory would need both shorter and longer annealing times in order to show how rapidly the initial stage takes place, and also to study the slow star-like relaxation stage. This could confirm that the brush in the spin coated sample is at equilibrium. Experiments on the latter time scale should be sensitive to whether the matrix is permanently cross-linked or a melt. Future experimental investigations could also study the effect of grafting density, and of introducing a favourable interaction between the grafted and matrix polymers. We propose to perform further experiments to investigate these questions.

CONCLUSIONS

We have measured segment density profiles of grafted chains by neutron reflectivity. In this way we have investigated the kinetics of penetration of a grafted polymer into a high molecular weight polymer matrix. Two methods for making bilayers, floating and spin coating the top layer, were used. Spin coating and annealing produces an initially diffuse interface between the matrix and the brush. This prevents formation of 'runners' at the substrate and so equilibrium can be reached more quickly. Floating and annealing produces a different profile, which we suggest corresponds to a metastable state.

The observation that the brush profile that is produced by annealing the initially sharp interface is different from the one produced by spin coating and annealing has important consequences for experiments on the dynamics of polymer chains at interfaces. It is common practice to produce bilayer samples by floating a polymer film on top of one previously cast on a substrate. Care must be taken in experiments in situations where a brush is present at an interface to ensure that the metastable state is not mistaken for the true equilibrium.

The observation of this metastable state is consistent with the theory of O'Connor and McLeish, and the simulations of Deutsch and Yoon. Comparison of the profile from a spin coated sample has been made with the profile from numerical solutions of the SCMF equations and good agreement was found. More careful experiments are needed to investigate the theoretical predictions in detail. In particular, very long annealing times are needed to study how the profiles change as the grafted layer moves from the metastable state to the true equilibrium conformation.

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