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The effect of matrix molecular weight on the kinetics of formation of end-adsorbed polystyrene layers from the melt

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The adsorption of carboxy-terminated deuterated polystyrene chains to a surface from a polymer melt has been studied using helium (3) nuclear reaction analysis. These chains are initially uniformly distributed in a matrix of (protonated) polystyrene. On annealing above the glass transition temperature they physically end-adsorb onto the native oxide layer on a silicon substrate. We have measured adsorbed amounts and concentration profiles of the adsorbed layer as a function of the annealing time and the molecular weight of the matrix. A depletion region is initially observed behind the adsorbed layer which persists for long times in some cases. The width and depth of the depletion layer depends strongly on the molecular weight of the matrix polymer and cannot be simply explained in terms of simple diffusion of the functionalized chains. Copyright © 1996 Elsevier Science Ltd.

(Keywords: end-functionalized polystyrene; polymer brush; kinetics)

INTRODUCTION

There has been much interest in recent years, both experimental[1-4] and theoretical[5-8], in developing an improved understanding of polymer layers in which chains are attached by one end to a surface (sometimes known as brushes). These systems are of considerable importance because of their many current and potential applications; examples include adhesives, lubricants, colloidal stabilizers and composite materials. Typically, the polymer is attached to the surface by a short block of adsorbing copolymer or by a functional group which exhibits an affinity for the surface. Several workers have investigated the equilibrium aspects of adsorbed polymer layers[2-4] but little has been done to study the kinetics of adsorption. In a previous paper[1], we examined both equilibrium (such as the sticking energy and adsorption isotherm) and dynamic behaviour of this system (the rate at which the adsorbed amount increases with annealing time). In this paper we extend the previous work by studying the shape of the volume fraction profile near the adsorbed layer as a function of annealing time and matrix molecular weight. We have used nuclear reaction analysis (n.r.a.) to measure direct depth profiles of the deuterium content of polymer films.

EXPERIMENTAL

All the polymers used in this work were purchased from Polymer Laboratories and have narrow molecular weight distributions ($M_w/M_n \leq 1.06$). Their characteristics are listed in *Table 1*. The n.r.a. samples were prepared by spin coating from toluene solutions of approximately 3% (weight) polymer to produce films 2500–3000 Å thick on a single crystal silicon substrate. Approximately 15% of the total polymer was carboxy-terminated deuterated polystyrene, dPS(COOH), and the rest was (conventionally terminated) protonated polystyrene, hPS. A range of different molecular weights were used for the protonated matrix polymer, from 52×10^3 to 2.88×10^6. The molecular weight of the functionalized polymer was 79 750. After spinning, the films were placed in a vacuum oven at 150°C for a range of annealing times from 15 min to 7 days. 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 a vacuum since the heat transfer to the polymer only takes place by conduction through the silicon wafer; secondly, temperature fluctuations arise when the oven door is opened.

The n.r.a. data were obtained by using the 2 MeV Van de Graaff accelerator at the E.P.S.R.C. device fabrication facility at the University of Surrey. This technique has been described in detail elsewhere[9,10]. The data were compared to fits obtained by convolving a Gaussian of f.w.h.m. = 400 Å (to allow for instrumental resolution) with simple models for the profile. The models usually consisted of one, two or three rectangular blocks. The best fits were obtained by using a Marquardt–Levenburg routine[11] to minimize the χ^2 parameter, subject to the constraint that the known total amount of deuterated

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Table 1 Characteristics of the polymers used in this study

Polymer	Abbreviation	M_w	M_w/M_n
Carboxy-terminated deuterated polystyrene	dPS(COOH)	79750	1.04
Protonated polystyrene	hPS (52 k)	52 000	1.03
	hPS (330 k)	330 000	1.04
	hPS (501 k)	500 800	1.06
	hPS (758 k)	758 000	1.05
	hPS (1.46 M)	1 460 000	1.06
	hPS (2.88 M)	2 880 000	1.06

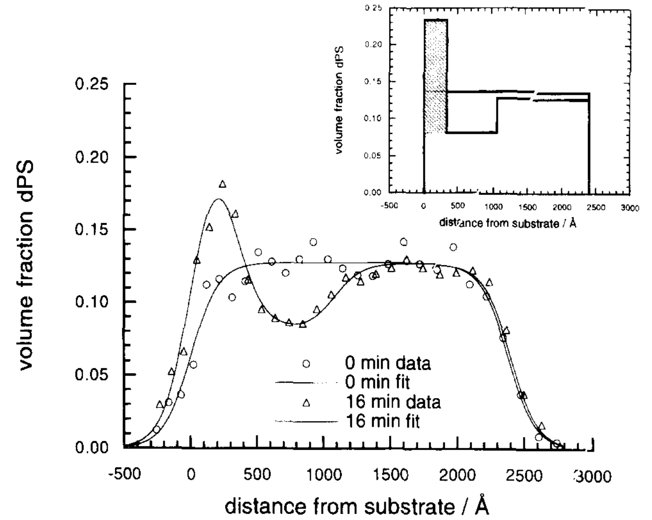

Figure 1 N.r.a. profiles for a sample of 14% dPS(COOH)/86% hPS (330 k) before (circles) and after annealing at 150°C for 16 min (triangles). The solid lines are fits obtained by convolving a model consisting of three rectangular blocks with a Gaussian instrumental resolution function. The inset shows the models used to produce the fits to the data. The surface excess, z^*, is calculated as the shaded area shown

polymer in the sample was conserved. The n.r.a. data for a typical sample are shown in *Figure 1*, together with the fit and the model. The data for an unannealed sample are also shown. The fit is insensitive to the precise height and width of the adsorbed layer as long as their product (the area) is unchanged. The surface excess, z^*, is therefore unaffected by the resolution and is calculated as the shaded area shown. The depleted region appears immediately behind the adsorbed layer.

RESULTS AND DISCUSSION

Figures 2–7 show the profiles for the 52, 330, 501, 758 k, 1.46 and 2.88 M matrices, respectively, for a range of annealing times. For clarity, the data points are omitted and only the best fits are shown. All the fits have values of $\chi^2 < 2$.

Approach to equilibrium

Figure 8 shows a plot of the surface excess against log time for all the samples. By the longest annealing times, no trace of the depletion layer could be observed in the profiles which suggests that equilibrium is being approached. *Table 2* gives the measured surface excess (z^*) for the longest annealing time for each of the molecular weights. The experimental error in the values of z^* is 10%. The numerical self-consistent mean field theory of Shull[12] predicts that the equilibrium adsorbed amount for a given sticking energy, initial bulk volume fraction and film thickness is independent of matrix

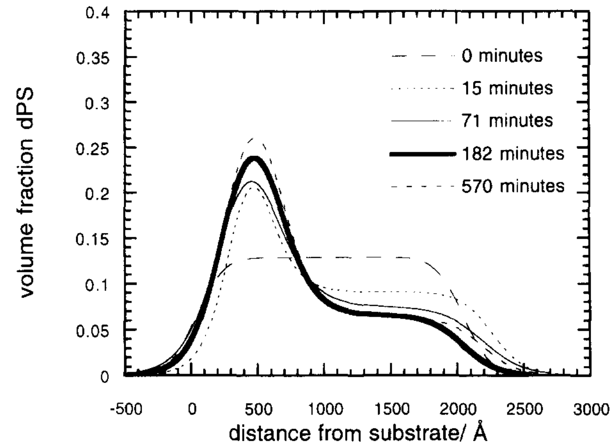

Figure 2 Fits to the n.r.a. profiles with a 52 k hPS matrix for samples annealed for 0, 15, 71, 182 and 570 min. For clarity, the data points are not shown

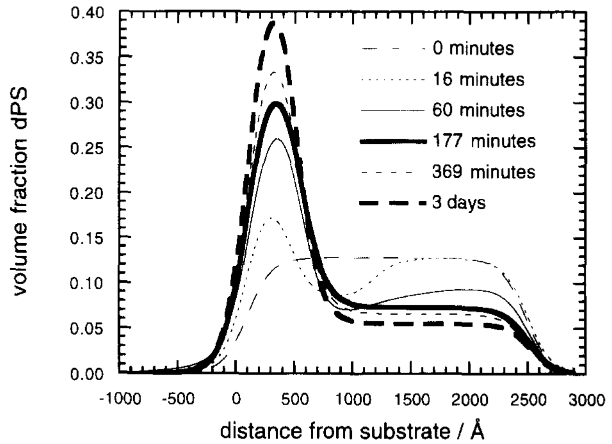

Figure 3 Fits for the 330 k matrix; annealing times 0, 16, 60, 177, 369 and 4320 min (3 days)

Table 2 Surface excesses for the long annealing time (3^a or 7^b days) samples

Matrix M_w	z^* (Å) 10%
330 k^b	176
501 k^a	126
758 k^b	150
1.46 M^b	187
2.88 M^a	81

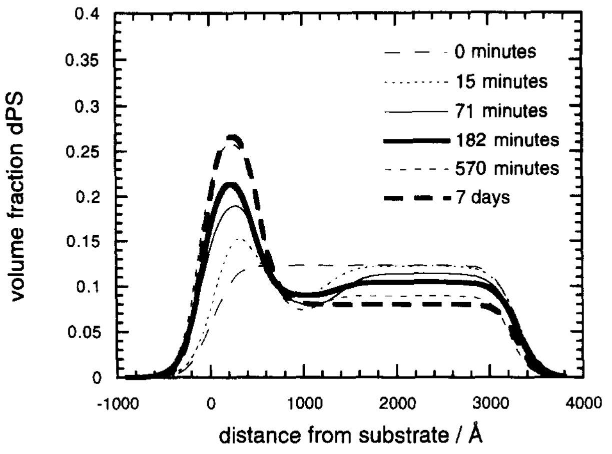

Figure 4 Fits for the 501 k matrix; annealing times 0, 15, 71, 182, 570 and 10080 min (7 days)

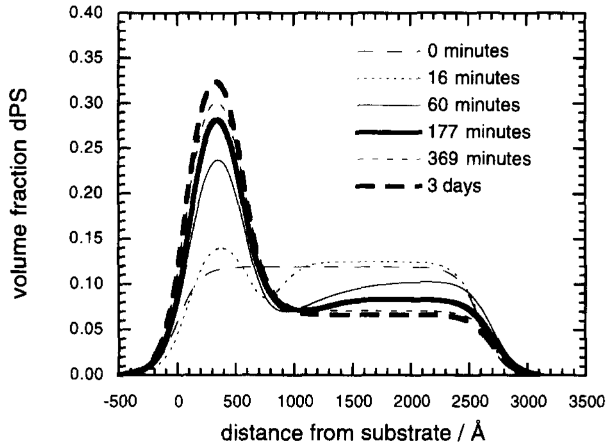

Figure 5 Fits for the 758 k matrix; annealing times 0, 16, 60, 177, 369 and 4320 min (3 days)

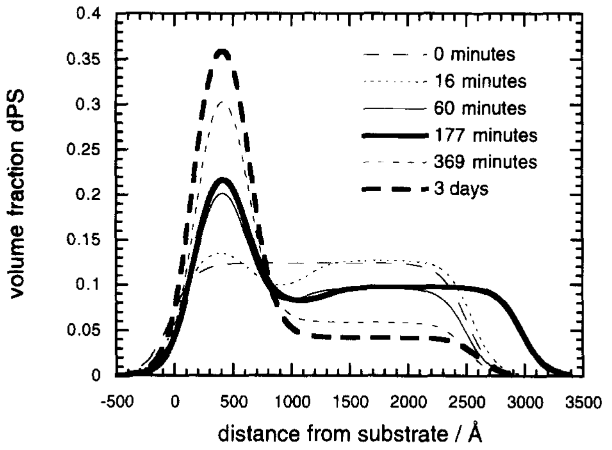

Figure 6 Fits for the 1.46 M matrix; annealing times 0, 16, 60, 177, 370 and 4320 min

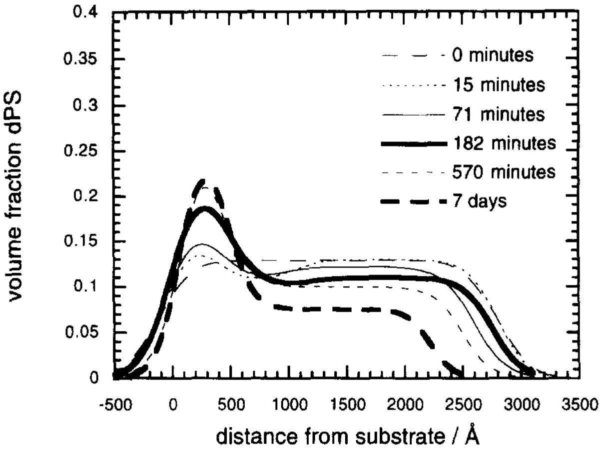

Figure 7 Fits for the 2.88 M matrix; annealing times 0, 15, 71, 182, 570 and 10080 min

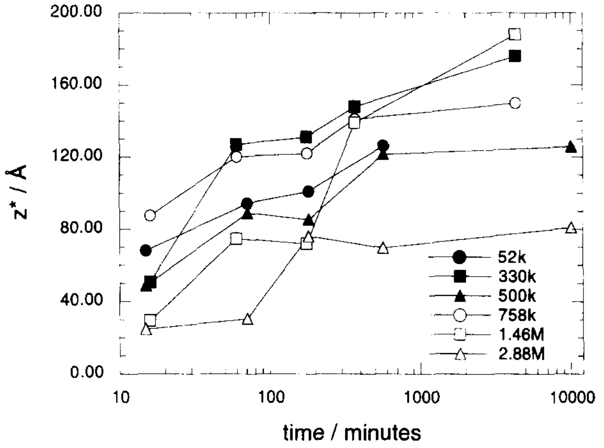

Figure 8 Plots of the surface excess z^* (Å) vs log (annealing time/min) for all the molecular weights

molecular weight if $N_{\mathrm{matrix}} > N_{\mathrm{brush}}$ (the 'dry brush' regime[12,13]). Here N is the number of segments per polymer molecule. This prediction has been experimentally verified in a slightly different situation[14]. Our results show quite large scatter, some of which can be accounted for by variations in film thickness and initial bulk volume fraction. However, the variation is too large to be attributed entirely to these (because the samples all had similar bulk volume fractions and thicknesses) so it seems that longer annealing times than used here are needed to reach equilibrium. The equilibrium situation has previously been studied in detail in any case[1–3].

Kinetics

The kinetics of formation of the grafted layer is a more interesting area for study. All the molecular weights show a monotonic increase in the adsorbed amount with annealing time. The slopes of these plots appear to be independent of molecular weight. The curves in *Figure 8* can be described by $z^* \sim t^{\nu}$ where $\nu = 0.18 \pm 0.07$. We attach no particular significance to this value, except to note the similar behaviour of all the molecular weights and also to point out that it is substantially different from $z^* \sim t^{0.5}$ which might be expected for simple diffusion governed kinetics. The vertical shift between the curves in *Figure 8* does not follow a simple trend with the molecular weight. The scatter between the data can at least partially be attributed to variations in film thickness and initial bulk volume fraction. However, it does appear that the surface excess builds up much more slowly in the highest molecular weight matrix. It should be noted that when a depletion layer is present, it can be difficult to obtain the surface excess accurately since several very different models can produce equally good fits to the data. For example, it is not always possible to accurately find the volume fraction of deuterated polymer in the depletion layer as the instrumental broadening of the peak at the substrate spreads into this layer. For samples with a depletion layer, the error in z^* is estimated as 15% (without a depletion layer it is 10%).

It is apparent from *Figures 2–7* that the molecular weight of the matrix has a strong effect on the concentration profile. The shapes of the profiles are particularly interesting. All the molecular weights except the lowest show a substantial depletion region behind the brush where the volume fraction of functionalized polymer is less than the bulk. This initially deepens and then slowly disappears as it is filled by material from the bulk on further annealing. The size of the hole does not show a simple monotonic variation with the molecular weight of the matrix and is most pronounced in the medium molecular weights (501, 758 k). This is surprising as the diffusion coefficient of the functionalized chains through the matrix should be independent of the matrix molecular weight (provided that it is greater than the entanglement molecular weight, ~18 k in PS).

The reason for the presence of the depletion region for short times is apparent. Initially the depletion layer is formed as functionalized chains near the wall adsorb so that for the shortest annealing time the adsorbed amount is equal to the amount of functionalized material removed from the depletion layer, and the volume fraction of functionalized chains in the bulk is unchanged from its initial value. However, the molecular weight dependence of the depletion layer and its shape cannot be explained in a simple manner. Consider first the 501 k sample. As annealing takes place, the adsorbed amount increases while the bulk volume fraction decreases; the width of the depletion layer does not change (~1000 Å from the edge of the adsorbed layer to the end of the depletion hole) but it does become shallower as the volume fraction in the bulk slowly decreases. Eventually the bulk volume fraction reaches the volume fraction in the depletion layer and behind the brush the concentration profile is flat. This behaviour is completely different from the time evolution of a depletion layer in a simple diffusion limited process where the rate limiting factor is the diffusive transport of functionalized chains from the bulk; in that case the width of the depletion region increases with time as[15] $\sim (Dt)^{1/2}$. For the other matrices (except the 52 k matrix where there is no depletion layer) the behaviour of the hole is similar. However, for the 330 and 758 k matrices there is one difference: after the initial formation of the depletion layer the hole does appear to become wider, i.e. more like the diffusion limited situation. In the 1.46 and 2.88 M matrices the depletion layer has an almost constant width but is much shallower than the medium molecular weights.

We can estimate the effective diffusion coefficient of the functionalized chains from in the 330 and 758 k matrices from the width of the depletion layer ($(Dt)^{1/2}$) after annealing for 60 min. Estimating the width as 1000 Å gives a diffusion coefficient of $3 \times 10^{-14}\,\mathrm{cm^2\,s^{-1}}$ which is not very different from the expected value of $\sim 6 \times 10^{-14}\,\mathrm{cm^2\,s^{-1}}$. This was calculated from previous measurements of the diffusion coefficient[16], by interpolating for molecular weight assuming the reptation model and for temperature assuming a WLF like temperature dependence. However, we cannot account for the other matrices in this way and there may be another process which influences the kinetics of adsorption of the functionalized chains.

It has recently been observed that the diffusion coefficient of polymers near a wall is lower than that of identical chains in the bulk[17], which is molecular weight dependent. This could have a significant effect on the kinetics of diffusion of matrix chains away from the wall which allows functionalized chains in. However, it is not certain that this effect would extend to the full width of the depletion layer, ~1000 Å from the wall.

In the previous paper[1] we showed that the kinetics of adsorption of the same end-functionalized chains in a 500 k hPS matrix (annealed at a higher temperature where no depletion layer was observed) did not conform to the predictions of a simple model. This model balanced the flux into the brush from the bulk with flux out of the brush[18]. A functionalized chain gains the sticking energy when it adsorbs, but has to overcome a potential barrier which arises from the stretching of the brush chains as the adsorbed amount increases. The model predicts that equilibrium would be reached very quickly (~1 h at the annealing temperature used in the current experiments), clearly much faster than is observed.

Another possibility has been suggested by Kramer[19], namely that the kinetics of the grafting reaction between the carboxy group and the oxide layer control the rate of brush formation. In that model, the build up of the brush reduces the concentration of functionalized ends near the wall. The reaction rate, therefore, slows down, and if the equilibrium strongly favours the grafted species, it is possible that equilibrium will never be reached in practical times. The rates of grafting predicted by this model can be much smaller than those from the diffusion limited model since they depend on the kinetic rate constant of the reaction at the interface.

Neither of these models can predict the depletion region, or that there should be any dependence of the adsorption on the molecular weight of the matrix. It is, therefore, clear that the models do not contain all of the essential physics of this problem. It is possible that a model which includes the generation and dissipation of stress in the molten matrix chains may predict the depletion region and the molecular weight dependence (Turner, M. S., personal communication).

CONCLUSIONS

Carboxy-terminated polystyrene strongly adsorbs from a polystyrene melt onto a silicon substrate. The kinetics of adsorption however are relatively slow, with annealing times of several days required to reach equilibrium. Samples were prepared for a range of matrix molecular weights and a substantial depletion layer was observed in all except the lowest molecular weight. The size and shape of the depletion layer depends on the matrix molecular weight whereas the rate of build up of the adsorbed layer does not appear to be strongly influenced by it. We are currently unable to explain this behaviour but we believe that a model which includes the relaxation of the matrix chains may account for it. We note that these results have important applications for the experimental study of the adsorption of polymer chains at interfaces in the melt.

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