Kinetics of formation of physically end-adsorbed polystyrene layers from the melt

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We have used neutron reflectivity and helium (3) nuclear reaction analysis to measure adsorbed amounts and concentration profiles of carboxy-terminated polystyrene chains in the melt, which are physically end-adsorbed onto the native oxide layer on silicon substrates. The excess of adsorbed chains at the substrate increases with annealing time, but more slowly than predicted by a model. We have measured the adsorption isotherm for this system. By comparison with numerical solutions of self-consistent field equations we deduce a sticking energy of 8.6 kT per molecule.

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

INTRODUCTION

There has been much interest in recent years, both experimental[1–3] and theoretical[4–7], 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. A polymer layer can bond to an inorganic phase via a head group while the tail entangles with the matrix polymer, e.g. filler particles in paints. 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. In this study, we use deuterated polystyrene chains terminated at one end with a carboxy group. We show that this end group drives substantial adsorption of the functionalized polymer to the interface with a silicon substrate from a blend of high molecular weight (conventionally terminated) polystyrene.

Numerical solutions of the self-consistent field (SCF) equations for grafted polymer layers have recently been reported[8]. SCF theory relies on the mean field approach[9], where the influence of the many other 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. By measuring the segment density profile of chains attached to a surface it is possible to test these calculations[10]. Neutron reflectivity (n.r.) is an ideal technique for this investigation since the contrast in neutron scattering lengths between hydrogen and deuterium gives high depth resolution. It is particularly powerful when used in conjunction with nuclear reaction analysis (n.r.a.). Although n.r.a. has poorer resolution, it provides a direct depth profile that eliminates the uncertainty which arises from the fact that models used to match reflectivity data may not be unique. Both n.r.[11] and n.r.a.[12,13] have been described in detail elsewhere.

In order to compare the efficacy of different end groups, it is helpful to measure the sticking energy of a functionalized chain (the energy gained when an end group adsorbs from the polymer melt). Previously this has been done by considering the adsorption as a chemical reaction at equilibrium[14]. We obtain a value of the sticking energy by comparison of the experimental adsorption isotherm with numerical solutions of the SCF equations.

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EXPERIMENTAL

All the polymers used in this work were purchased from Polymer Laboratories. Their characteristics are listed in *Table 1*. Monodispersed carboxy-terminated deuterated polystyrene (dPS(COOH)) was prepared by anionic polymerization, the living chains being terminated with solid carbon dioxide. This produced a yield of about 85% dPS(COOH). The samples were prepared by spin-coating from toluene solutions of approximately 3 wt% polymer. For the kinetics experiments, approximately 15% of the total polymer was carboxy-terminated. After spinning, the films were placed in a vacuum oven for a range of annealing times. The reflectivity data were taken at room temperature on the CRISP time-of-flight reflectometer at the ISIS facility, Rutherford Appleton Laboratory (Didcot, UK). The ion beam data were obtained by using the 2 MeV van de Graaff accelerator at the SERC device fabrication facility at the University of Surrey (Guildford, UK). Since it is not possible to perform both types of experiment on the same sample, owing to limitations on sample size in the n.r.a. beam line, identical samples were prepared for each technique. The reflectivity data were analysed by a simplex fitting routine to minimize the χ^2 parameter, subject to the constraint that the total amount of deuterated polymer in the sample was conserved.

Table 1 Characteristics of the polymers used in this study

Polymer	Abbreviation	M_w	M_w/M_n
Carboxy-terminated deuterated polystyrene	dPS(COOH)	79 750	1.04
Protonated polystyrene	hPS	500 800	1.06

RESULTS AND DISCUSSION

Study of the kinetics

Samples of 15% dPS(COOH)/85% protonated polystyrene (hPS) were annealed in a vacuum oven at 184 ± 3°C for times ranging from 15 min to 24 h. A further sample was sealed in glass under argon and annealed in another oven for 7 days. This was necessary to prevent degradation of the polymer film, which can sometimes occur for samples annealed in the vacuum oven for a long period of time. The n.r.a. profile for the 24 h sample is shown in *Figure 1*, and is compared with the profile for an unannealed sample. The solid line is a fit to the data obtained by convolving a Gaussian of full width at half maximum = 600 Å to simulate instrumental resolution, with the square block model shown. This simple model works well as the resolution is not sufficient to show more detailed features of the brush profile. The fit

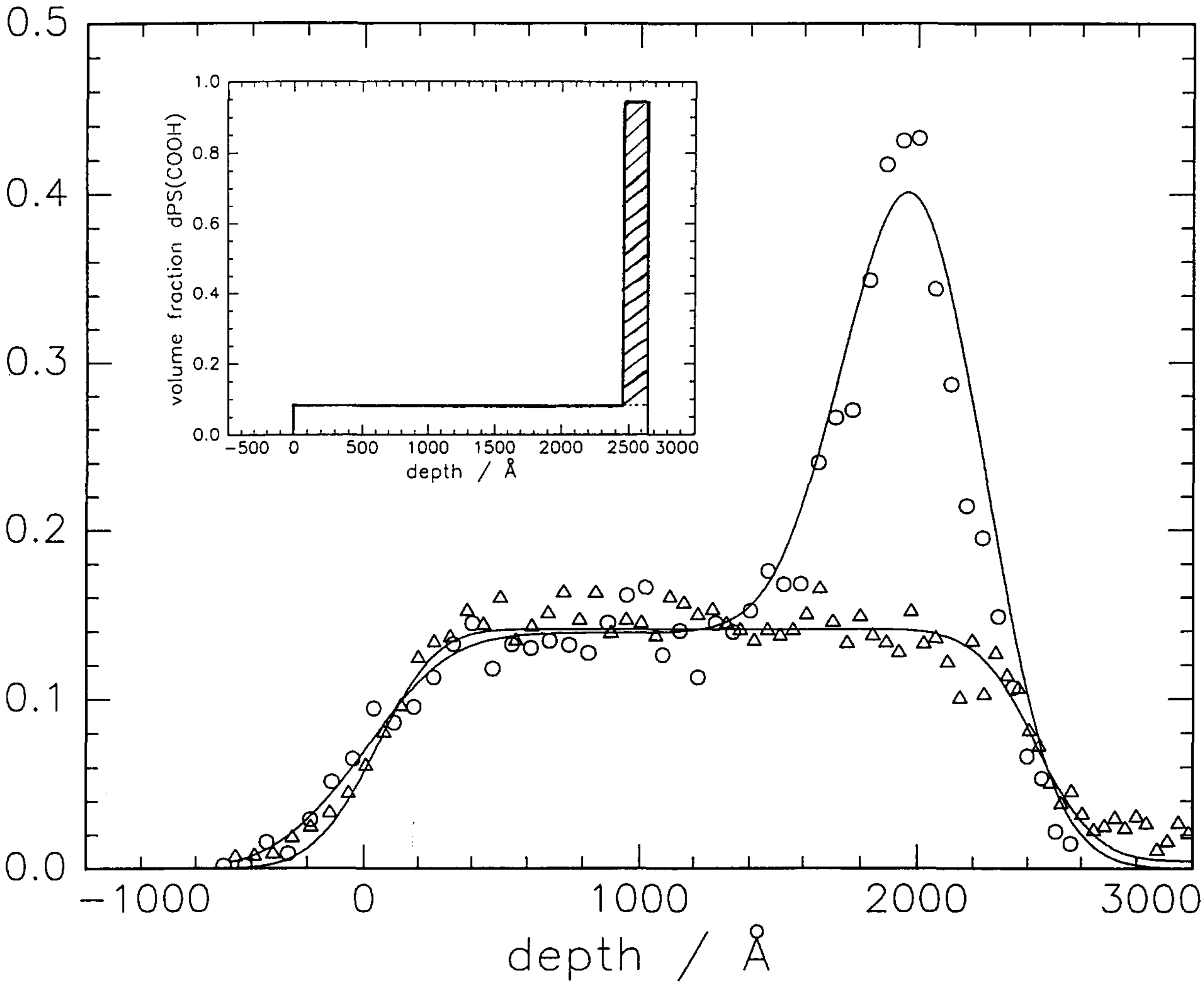

Figure 1 N.r.a. profiles for a sample of 15% dPS(COOH) before annealing (△), and after annealing at 184°C for 24 h (○). The solid lines are fits obtained by convolving a two-block model with an instrumental resolution function. The inset shows the model used to produce the fit to the data; the surface excess, z^*, is calculated as the shaded area

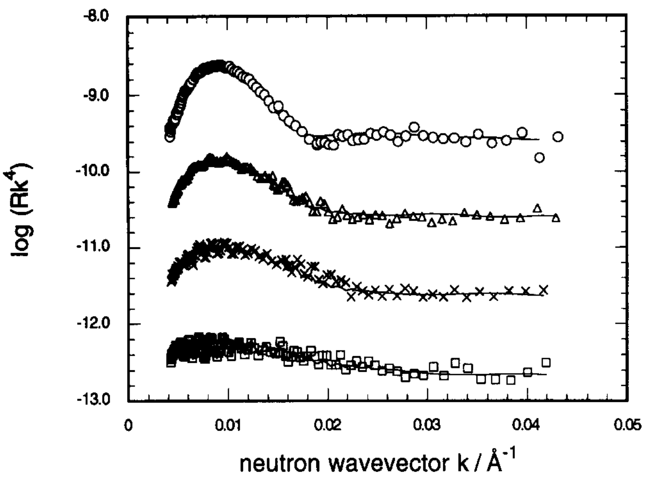

Figure 2 Neutron reflectivity data for samples annealed for 1 h (□), 4 h (×), 24 h (△) and 7 days (○). The data have been vertically shifted for clarity. The solid lines are fits obtained from the profiles in *Figure 3*

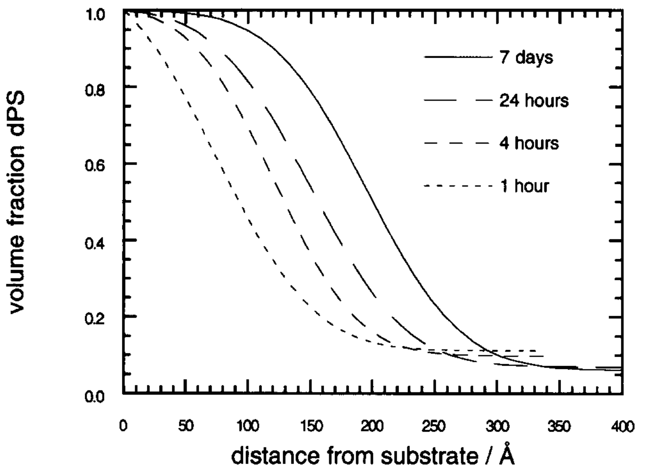

Figure 3 Error function profiles used to produce the fits in *Figure 2*

is insensitive to the precise height and width of the second block 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 inset.

Reflectivity data from a set of samples annealed for the same range of times are shown in *Figure 2*. The solid lines are fits obtained using an error function profile:

$$\phi(z)=\frac{(\phi_0-\phi_\infty)}{2}\left[1+\mathrm{erf}\left(\frac{z-h}{w}\right)\right]+\phi_\infty \qquad (1)$$

where ϕ_0 is the volume fraction of dPS(COOH) at the substrate, h is the height of the brush and w is a measure of the width of the interface between the brush and the melt. The best-fit profiles are shown in *Figure 3*. The fits have normalized chi-squared values in the range 1.5–5. The values of z^* from n.r. are consistent with those from the n.r.a. experiments.

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; and secondly, temperature fluctuations arise when the oven door is opened. In order to explore shorter times, the n.r.a. experiments were repeated on samples annealed at 120 and 150°C, where the diffusion coefficient of the dPS(COOH) is smaller than at 184°C. *Table 2* shows predicted diffusion coefficients for the functionalized chains in this system. The expected values were found from previous measurements of the diffusion coefficient[15], by interpolating for molecular weight assuming the reptation model[16] and for temperature assuming a Williams–Landel–Ferry (WLF)-like temperature dependence[17]. No segregation was observed in the samples annealed at 120°C (the longest annealing time at each of these temperatures was 4 days). The best-fit profiles to the n.r.a. data for the 150°C samples are shown in *Figure 4*. A substantial depletion layer is apparent for annealing times up to 4 h (the samples annealed at 184°C did not have a depletion layer). The predicted diffusion coefficient is such that dPS(COOH) chains would be expected to diffuse a distance of 100 Å in about 20 s at this temperature, so we would expect the depletion layer to be filled rapidly by deuterated polymer from the bulk. The persistence of the depletion layer for times up to 4 h suggests that diffusion is slowed down considerably from the expected rate.

We have measured the diffusion coefficient of dPS(COOH) chains by performing n.r.a. experiments on bilayers of 10% dPS(COOH) and pure hPS. Samples were annealed at 181°C for times ranging from 1 min to 1 h and the diffusion coefficients were calculated by fitting an appropriate series solution of the diffusion equation to the n.r.a. data, allowing for instrumental broadening. The self-diffusion coefficient was found to be $(5\pm2)\times10^{-13}\,\mathrm{cm^2\,s^{-1}}$, compared with an expected value of $(20\pm2)\times10^{-13}\,\mathrm{cm^2\,s^{-1}}$. The reduction by a factor of

Table 2 Predicted diffusion coefficients of dPS (M_w 79 750) in hPS (M_w 500 800)

Temperature (°C)	Diffusion coefficient (cm^2 s^{-1})	Time to diffuse 100 Å
120	$(1.3\pm0.3)\times10^{-16}$	2 h
150	$(5.8\pm1.0)\times10^{-14}$	20 s
184	$(2.3\pm0.5)\times10^{-12}$	0.5 s

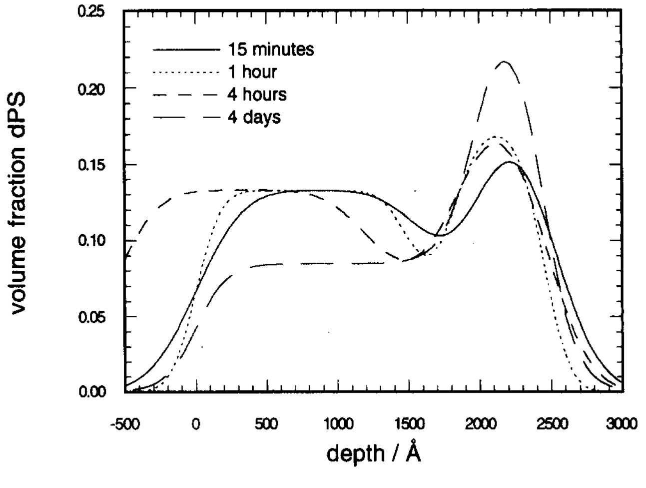

Figure 4 Best-fit profiles to the n.r.a. data for samples annealed at 150°C

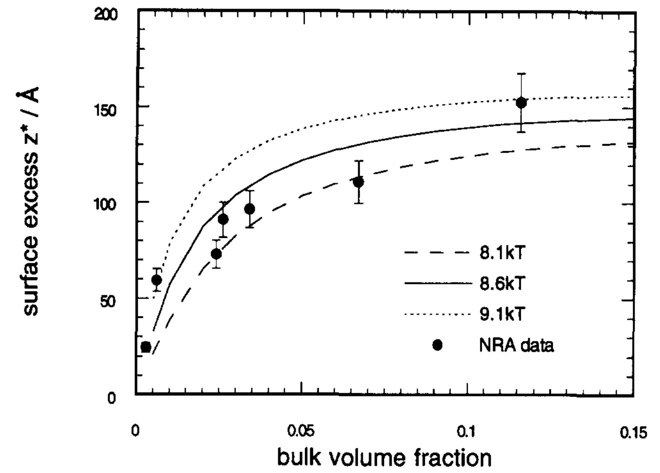

Figure 5 Plot of surface excess *versus* bulk volume fraction: the lines are adsorption isotherms for SCF profiles, and the data points are from n.r.a. experiments on samples annealed for 6 days at 184°C. These suggest a value of 8.6 ± 0.5 kT for the sticking energy

about four is consistent with a doubling of the molecular weight owing to dimerization of the dPS(COOH) chains, although Fetters *et al.*[18] have found little aggregation in a similar system. This explanation could be checked by small-angle neutron scattering experiments.

Measurement of the adsorption isotherm

The adsorption isotherm, i.e. the equilibrium surface excess of brush polymer as a function of its bulk concentration, can provide information on both the sticking energy and the mechanism for brush formation. N.r.a. experiments were performed on samples ranging from 1 to 15 wt% dPS(COOH), annealed at 184°C for 6 days. The surface excess is plotted against bulk volume fraction in *Figure 5*. The solid lines are isotherms obtained from numerical SCF theory, shown with their sticking energies. By comparing the n.r.a. experiments with the SCF isotherms, we obtain a sticking energy of 8.6 ± 0.5 kT. This value of 8.6 ± 0.5 kT per molecule at 184°C corresponds to an enthalpy of 7.8 ± 0.5 kcal mol^{-1} which is in excellent agreement with the result of Zhao *et al.*[14] of 7.4 kcal mol^{-1} for a similar system.

Time–temperature correspondence

By making use of time–temperature correspondence, it should be possible to collapse data obtained at different annealing temperatures onto a single curve. In general it should be possible to express the surface excess as:

$$z^*(\phi_\infty, T, t) = F(\phi_\infty)G(T)H(t) \qquad (2)$$

where F, G and H are unknown functions. If we can determine $F(\phi_\infty)$, i.e. the adsorption isotherm, and $G(T)$, the temperature dependence, then we should be able to combine the sets of data for the kinetics obtained at different annealing temperatures. $F(\phi_\infty)$ has been determined in the previous section. Zhao *et al.*[14] have estimated the combination FG by measuring the equilibrium surface excess at four different temperatures between 108 and 235°C. By considering the adsorption process as an equilibrium between end-functionalized polymer at the substrate and in the bulk they obtained:

$$z^*_{\mathrm{eqm}} = c\phi_\infty \exp\left(\frac{-\Delta H}{k_B T}\right) \qquad (3)$$

where c is an unknown constant with dimensions of length. From their data, plotted as $\ln(z^*/\phi_\infty)$ against $1/T$, they estimated the enthalpy of adsorption, ΔH and the entropy change ΔS (which was found to be negligible). This approach appears to be in conflict with our measured adsorption isotherm, which is not linear as equation (3) implies. The approach of Zhao *et al.*[14] does not take into account the fact that it becomes harder for a chain to adsorb as the brush builds up and the chains are forced to stretch out. The linear variation of z^* with ϕ_∞ in equation (3) reflects this. However, a plot of $\ln(z^*/\phi_\infty)$ against $1/T$ is relatively insensitive to errors in the value of z^*/ϕ_∞. Since the value of z^*/ϕ_∞ changes only by a factor of about two over the range of bulk volume fractions sampled by their experiments, the non-linearity of the isotherm should not greatly affect this plot. Thus it is not entirely surprising that the model still fits their data, despite its deficiency.

In our kinetics experiments the starting composition of all the samples used was 15% dPS(COOH), so that ϕ_∞ varied over only a small range (0.1–0.15). *Figure 5* shows that in this region the dependence of z^* on ϕ_∞ is weak. It will therefore have only a small contribution to the scaling, which is dominated by the temperature dependence. We can therefore safely use equation (3) to scale z^*, i.e.

$$z^* \to \frac{z^*}{c\phi_\infty \exp\left(\frac{-\Delta H}{kT}\right)} \qquad (4)$$

Similarly the transformation

$$t \to \frac{Dt}{\left[c\phi_\infty \exp\left(\frac{-\Delta H}{kT}\right)\right]^2} \qquad (5)$$

where D is the diffusion coefficient of dPS(COOH) chains in the hPS matrix, makes t dimensionless. *Figure 6* shows a log–log plot of surface excess against annealing time. Since c is unknown, the 150°C data (z^* and t) have simply been multiplied by the ratio of the scaling factors at 184 and 150°C so that the whole plot should correspond to 184°C. The data indeed collapse onto a single curve. The error bars are slightly larger than the plotted symbols, and there is also some uncertainty in the scaling factor which is difficult to quantify since Zhao *et al.* do not give

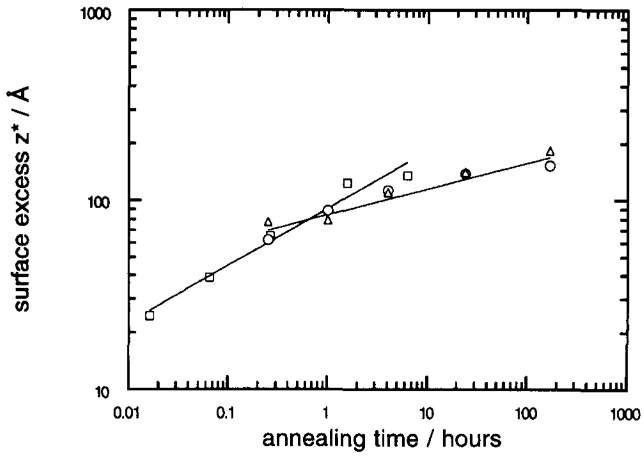

Figure 6 Log–log plot of surface excess, z^*, against time for samples annealed at 150°C (□, n.r.a.) and 184°C (○, n.r.a.; △, n.r.). The annealing times for the 150°C points have been scaled as described in the text

any estimate of the error in their value for ΔH. There is a change in slope from $t^{0.3}$ to $t^{0.13}$ when the surface excess corresponds to a monolayer of 'mushrooms'. This may correspond to an increasing energy barrier for adsorbing chains to penetrate as the brush chains begin to overlap and are forced to stretch out away from the wall. This is considered further in the next section.

A model for the kinetics of brush formation

Brush formation has been described as a two-stage process[5,6,19]. The first rapid stage is governed by diffusion while the slower build-up of the brush is controlled by the stretching of brush chains as they become more densely packed. Semenov[5] has formulated equations that govern the kinetics of brush formation, in the context of block copolymer segregation to the interface between two immiscible homopolymers. We have adapted his argument to end-functionalized polymers at a wall.

Consider end-functionalized polymer chains uniformly distributed in a matrix polymer. At very early times, when $z^* \ll R_g$ (i.e. the grafting density is low; R_g is the unperturbed radius of gyration of the dPS(COOH) chains), any functionalized chain which comes close to the wall will be pulled almost immediately into the brush because of the large energy gain. The volume fraction of free functionalized chains ϕ_f near to the wall is then very small, i.e. there will be a depletion layer. At this stage, each brush chain is essentially independent of the others and forms a 'mushroom', and the surface excess is given by

$$z^* = \frac{2}{\sqrt{\pi}} \phi_0 \sqrt{Dt} \tag{6}$$

Equation (6) is valid for $z^* \ll R_g$. As more chains adsorb, the anchored chains begin to interact and form a brush in which they are stretched in order to minimize their unfavourable interactions. For dense brushes ($z^* \geqslant R_g$), the boundary condition must be changed. Now in order to penetrate the brush the chain has to overcome a potential barrier U which arises from the loss of entropy caused by stretching of the brush chains. This is approximately given by[5]:

$$U = \frac{\pi^2}{16} \frac{\sigma^2 N}{a^2} = \frac{\pi^2}{16} \frac{z^{*2}}{Na^2} = \frac{\pi^2}{16} \frac{z^{*2}}{R_g^2} \tag{7}$$

where σ is the grafting density and N is the degree of polymerization of the dPS(COOH) chains. Now the flux of free chains into the brush J_+ is:

$$J_+ = \left(\frac{\partial z^*}{\partial t}\right)_+ = \frac{D}{R_g} \phi_f(0) \exp(-U) \tag{8}$$

The factor D/R_g is included for dimensionality, but is not exact. For a large adsorbed amount, the exponential term dominates. Ligoure and Leibler[19] have expressed the flux out of the brush J_- as:

$$J_- = \frac{D_R}{l} \frac{z^*}{a} \exp(-\Delta) \tag{9}$$

where D_R is the Rouse diffusion coefficient, Δ is the sticking energy (i.e. the energy needed to remove a carboxy group from the oxide layer on the substrate), and the factor D_R/l is included for dimensionality. This may be interpreted as an 'attempt frequency' multiplied by the distance that the end group has to move away from the wall to break the bond (cf. diffusion of atoms on a lattice). We can use the segment length a as the length l and estimate D_R by considering the Rouse model for the motion of the chain end. Finally, we can combine equations (7), (8) and (9) to obtain:

$$\frac{\partial z^*}{\partial t} = \frac{D}{R_g} \phi_f(\infty) \exp(-U) - \frac{D_R z^*}{a^2} \exp(-\Delta) \tag{10}$$

This equation can be solved numerically using a finite difference method. It should be pointed out that this treatment is approximate for two reasons: firstly, numerical factors of order one have been omitted from both terms in the right-hand side of equation (10); and secondly, the initial condition is approximate—the crossover between the diffusion-limited regime (when the adsorbed chains are mushrooms) and the brush regime is not sharp. In fact there is an intermediate regime where the brush chains interpenetrate, but are not strongly stretched (the 'screened brush' regime)[10]. The above treatment overestimates the stretching energy of chains penetrating the brush in this regime (i.e. for $z^* < \sim 2R_g$, when the chains are not yet strongly stretched).

By setting the left-hand side of equation (10) equal to zero, we can obtain the equilibrium surface excess as a function of the bulk volume fraction (the adsorption isotherm). The predicted equilibrium surface excess for an initial dPS volume fraction of 0.15 with the measured value for Δ is 62 Å, which is much lower than the experimental or numerical SCF values (~ 150 Å). However, if we allow a numerical factor of 20 in the term for the flux into the brush, the equilibrium surface excess becomes ~ 143 Å, which is much closer to the correct value. A numerical factor of 20 is not implausible since there are missing factors (of order one) in the expressions for both the flux into and out of the brush. It is not possible to justify the numerical factor in a rigorous way, so no firm conclusions may be drawn from this.

The predicted time to reach equilibrium obtained by numerically solving equation (10) (~ 3 min) is much less than the experimental value (> 24 h). Even allowing for dimerization of the end-functionalized polymer, which reduces the self-diffusion coefficient by a factor of four, we cannot account for the discrepancy between the experimental and predicted time-scales. The diffusion coefficients would need to be reduced by about two orders of magnitude in order to match the experimental results. One possible explanation is that if the end-functionalized polymers have dimerized, then they must dissociate before they can adsorb to the substrate. Thus there would be an extra energy barrier which the chains must overcome before they can adsorb, so the build-up of the brush would be slower. Since it is not known what proportion of the end-functionalized chains have dimerized (if any), it is not easy to include this in the model.

We can see further shortcomings of this simple theory by considering the scaling behaviour. Since the scaling arguments worked for the experimental data, we might expect the same arguments to apply to the predictions of the model. The equilibrium surface excess was calculated from equation (10) for a range of temperatures, and scaled according to equation (4). We assume that the free energy of adsorption is purely enthalpic, as suggested by Zhao *et al.*[14], so that it varies inversely with temperature. The points did not reduce to a single value, which would be the case if the model were correct. *Figure 6* is consistent with a reduction in the rate of build-up in the brush at $z^* \sim R_g$. However, the initial $t^{0.3}$ dependence is different

Table 3 Summary of best-fit error function profiles

Annealing time	ϕ_0	Height (Å)	Width (Å)	z^* (Å)
15 min	1.0	74.3	84.7	77.4
1 h	1.0	75.5	87.3	79.0
4 h	1.0	120.8	75.0	110.5
24 h	1.0	150.0	85.8	140.7
7 days	1.0	195.4	85.3	183.4

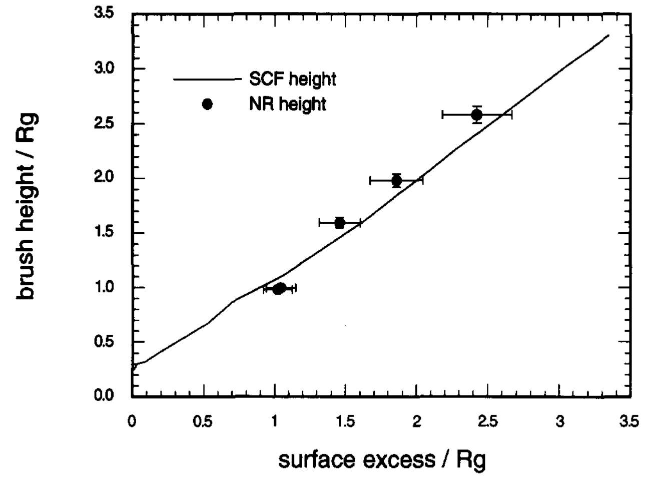

Figure 7 Plot of brush height against surface excess. The points are obtained from the profiles in *Figure 3* and the solid line is obtained from SCF profiles

from the expected $t^{0.5}$ for a diffusion-limited process. To summarize, we conclude that the theory as it stands cannot account for the experimentally observed kinetics. The reason for the discrepancy is not clear at present, although we suggest that dimerization of the functionalized polymers may be contributing. The amount of dimerization (if any) could be investigated by small-angle neutron scattering experiments.

Investigation of the brush profile

Neutron reflectivity experiments allow the detailed shape of the brush to be determined. The segment density profiles obtained from the n.r. experiments can be described by error functions, which are experimentally indistinguishable from hyperbolic tangents. (By choosing the value of the parameter a to be $(2/\sqrt{\pi})$, such that the gradients are equal at $x=0$, $\tanh(ax)$ and $\mathrm{erf}(x)$ are almost identical.) The width of the interface between the brush and the bulk remains approximately constant on annealing, while the height of the brush and the surface excess increase as the grafting density increases and the chains are forced to stretch. These parameters are summarized in *Table 3*. The volume fraction of brush polymer at the substrate remains at 1 throughout. *Figure 7* shows the surface excess as a function of brush height. The points are data from reflectivity experiments while the solid line was obtained for dry brushes by Shull[8]. Although the samples annealed for short times have not reached equilibrium, a local equilibrium should exist between the brush and the polymer close to it[20]. Therefore it should be possible to match the n.r. profiles with numerical SCF profiles by reducing the surface coverage, corresponding to a shorter annealing time. Two reflectivity profiles (for the 24 h and 1 h anneals) together with the best-matched SCF profiles are shown in *Figure 8*. We have obtained very good matches for the 7 day and 24 h samples. However, for the shorter annealing times the matches become less good. This may be because the local equilibrium approximation is not valid.

CONCLUSION

Carboxy-terminated polystyrene strongly adsorbs from a polystyrene melt onto a silicon substrate. The kinetics of adsorption, however, are relatively slow. A model adapted from one due to Semenov, which allows for the energy barrier for chains entering a dense brush, cannot account for the experimental kinetics. A substantial depletion layer was observed for samples annealed at 150°C, which suggests that the diffusion coefficient of dPS(COOH) chains is lower than the diffusion coefficient of conventionally terminated chains of equal molecular weight. Measurements of the diffusion coefficient are consistent with dimerization of the end-functionalized chains. Dimerization may contribute to the slow kinetics, but the decrease in the value of the diffusion coefficient alone is not sufficient.

Comparisons have been made with numerical self-consistent field profiles. The brush profiles are described by error functions, and we have found good agreement between SCF and experimental brush profiles when the grafting density is high. The adsorption isotherm has been determined and the sticking energy has been estimated as $8.6 \pm 0.5\,\mathrm{kT}$.

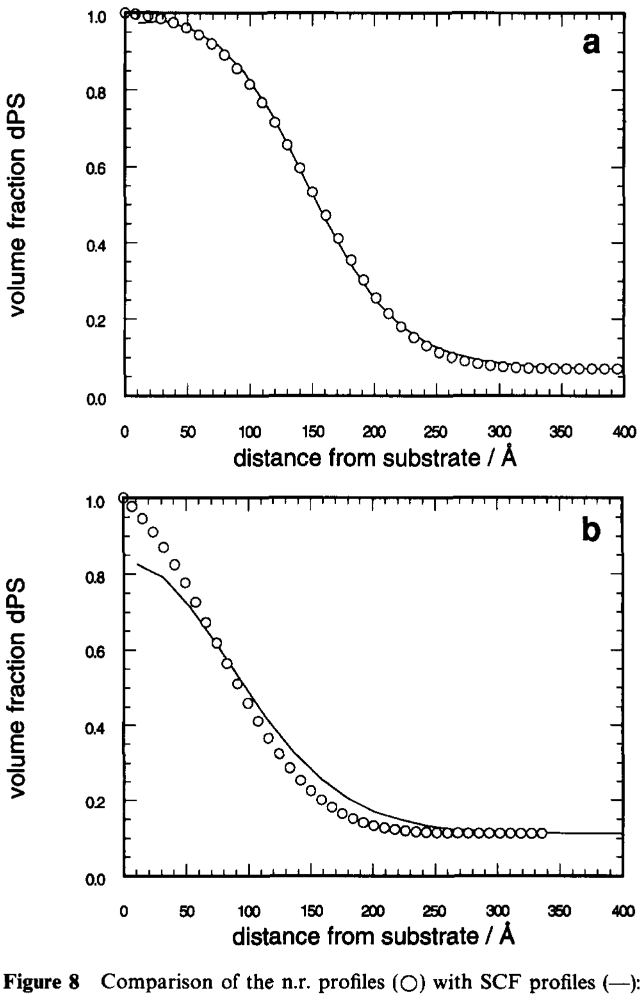

Figure 8 Comparison of the n.r. profiles (○) with SCF profiles (—): (a) 24 h (large sticking energy); (b) 1 h (small sticking energy)

The results have important implications in systems where both polymers and inorganic materials are present. We have shown that the adsorption behaviour is dominated not by the bulk of the polymer chain, but by one small group. Carboxy groups may be present in polymers unintentionally, since they could be formed in the termination step of polymerization or by oxidation. This would lead to the segregation of the polymer at interfaces, greatly affecting the properties of the system, which may or may not be desirable. For example, by simply changing the termination step to introduce a carboxy group the adhesion between polymer and filler particles in a composite material could be increased, leading to a much improved product.

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