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Influence of Matrix Molecular Weight on a Brush - Like Surface Layer Formed by a Polymer Functionalised at Both Ends

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Abstract. — Deuteropolystyrene has been functionalised at each end by fluorosilane groups, the polymer obtained had a relative molar mass of 98×10^3 . Thin films of this polymer mixed with unfunctionalised hydrogenous polystyrene have been prepared and the blends annealed to equilibrium at 413 K. The distribution of the end functionalised deuteropolymer was obtained by neutron reflectometry and a range of molecular weights of the hydrogenous polystyrene matrix has been used. In all cases the deuteropolystyrene was preferentially located at the air-polymer interface to an extent which was far greater than that for unfunctionalised deuteropolystyrene in the same hydrogenous matrices. From the near surface depth profiles obtained, the surface excess, surface volume fraction and thickness of the end functionalised deuteropolystyrene rich layer have been obtained as a function of the equilibrium concentration of end functionalised deuteropolystyrene. These parameters have been compared with the predictions of scaling theory for brush like layers of polymers attached to a surface. The surface layer thickness and average volume fraction of the surface layer display stretched wet brush behaviour which is not expected for end functionalised polymers on the basis of the molecular weights explored. The possibility that local grafting densities are significantly higher than the average value is discussed. The shape of the near surface depth profile has been fitted using a self consistent field theory using the “sticking energy” of the fluorosilane groups as the only adjustable parameter. Fits of reasonable quality were obtained and using this sticking energy the surface volume fractions and normalised surface excess parameters have been calculated and compared with those obtained experimentally. Good agreement between surface volume fractions is obtained, but the agreement between normalised surface excess values becomes increasingly worse as the relative molar mass of the hydrogenous matrix increases.

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Introduction

Attachment of polymers to surfaces or interfaces under conditions where the majority of units in the polymer chain are distant from the interface is of importance in many situations [1]. Steric stabilisation of particulate colloidal dispersions and the stabilisation of emulsion droplets are two such areas which have been intensively studied for many years. More recent subjects where such polymer attachment is also highly relevant are adhesion [2,3] and the use of copolymers as compatibilisers of immiscible homopolymers [4-6]. Although each of these areas has been discussed from their particular viewpoint, each has a major factor in common, *i.e.* the attached polymer forms a “brush like” layer at the surface or interface. A polymer brush is defined as the layer formed by the attachment of polymer molecules by one anchoring point (generally at one end of the molecule) to a surface or interface. Beginning with the seminal papers by Alexander [7] and de Gennes [8] much attention has been paid to such brush layers both experimentally and theoretically. Clearly the ability of the anchoring group to function effectively is paramount, however the nature of the surrounding matrix by which the brush molecules are surrounded also influences the arrangement the polymer segments adopt in the brush layer.

The scaling description developed by de Gennes [8] is particularly transparent in setting out the influence of surrounding matrix and areal density (*i.e.* number of molecules per unit area of interface) of attached or grafted molecules on the extension of the molecules from the plane of attachment. Subsequently, analytical expressions have been developed for the distribution of segments normal to the interface when low molecular weight solvents constitute the surrounding matrix [9].

Scaling law descriptions were preceded by the Self Consistent Field (SCF) approach developed by Scheutjens and Fleer [1,10,11]. The major difference (apart from numerical exactness) from the scaling laws is that there is no a priori assumption of the shape of the concentration profile of polymer normal to the grafted surface, this is determined by the various contributions to the free energy. Although such SCF calculations can be computationally intensive, they have been brought to a high degree of sophistication and a notable extension to grafted polymers surrounded by a polymeric matrix has been made by Shull [12].

The majority of experimental studies of polymer brushes have been made on polymer molecules grafted to solid substrates [13-22] (generally silicon or mica). A significant amount of the published work has dealt with the results from the force balance where the force-distance curve obtained has been compared with that predicted by the various theories [23-29]. A particularly relevant study was carried out using small angle neutron scattering on porous silica containing grafted polymer [30] which followed closely on earlier work where polymer stabilised colloidal dispersions were used [31,32]. Notwithstanding the pertinence of such results to “real” situations, it is evident that the extraction of the concentration profile of polymer normal to the surface is by no means straight forward.

Where the grafted surface is planar, the number of applicable techniques multiplies and in some cases the data can be analysed more easily. Ellipsometry, ATR FTIR and neutron and X-ray reflectometry [33,34] may all be and have been applied to solid or liquid surfaces. Ion beam methods (*e.g.* Forward Recoil Spectrometry (FRES) and Nuclear Reaction Analysis (NRA)) being high vacuum methods can be applied to solid samples [20,35] and in this respect are similar to the “classical” techniques of SIMS and XPS. Determination of volume fraction profiles of adsorbed or grafted polymer melts in amorphous matrices has generally been done by either ion beam analysis or Neutron Reflectometry (NR) methods. The majority of such studies describe grafting at the solid substrate-polymer interface, only two are concerned with equilibrium grafting at the air-polymer interface. Clarke *et al.* [17] have used the widest range

of molecular weights in their investigation of the effect of matrix molecular weight on the brush layer profile. However only one grafting density, σ , was used and they point out that the conditions used do not correspond to equilibrium grafting, *i.e.* where ungrafted polymer is in equilibrium with the bulk mixture. Indeed, Liu *et al.* [21] suggest that at the grafting density used, the grafted chains must be distorted from ideal statistics. Nonetheless, these results showed that even in these highly grafted systems, the matrix polymer had a finite volume fraction at the grafted surface.

In an earlier paper [36] we discussed the near surface volume fraction depth profiles obtained for a fluorosilane terminated deuterio-polystyrene mixed with hydrogenous polystyrene. The fluorosilane group forces attachment at the air-polymer interface because of its low surface energy and results were discussed in terms of self consistent field theory. We discuss here the influence of placing fluorosilane groups at both ends of the deuteropolystyrene and the role of the molecular weight of the hydrogenous polystyrene matrix. Throughout the following discussion, grafting is to the air-polymer interface and only equilibrium grafting is discussed and hence “sticking energies” extracted from the self consistent field analysis are true values rather than “forced” values to give agreement of theoretical predictions with data in the absence of equilibrium grafting.

Theoretical Background

We outline here the scaling law predictions for the thickness of the grafted layer and follow this with a brief description of the self consistent field approach.

The scaling analysis considers grafted polymer molecules with a statistical step length, a , and degree of polymerisation, N , the tails of which are in contact with surrounding “solvent” of degree of polymerisation, P . Regimes of different behaviour are defined in terms of the grafting density, σ . When this is low and the volumes pervaded by the individual grafted molecules do not overlap, the grafted chains have ideal statistics. The grafted molecules are viewed as mushroom like regions, the radius of the mushroom being $N^{1/2}a$, this is also the thickness, h , of the layer. The upper limit to σ which defines this region is $\sigma \leq N^{-1}$. Above this value of σ the grafted molecules begin to overlap but initially they do not stretch and the layer thickness is still the ideal value of $N^{1/2}a$. This region is defined by an upper grafting density of $PN^{-3/2}$.

For higher grafting densities (up to $\sigma = P^{-1/2}$) even though the excluded volume interactions between the grafted molecules are screened out by the polymeric matrix, the molecules have to stretch because of the need to satisfy space filling requirements. As the grafting density approaches 1, then the matrix chains become increasingly expelled from the region occupied by the brush layers. In this “dry” brush regime it is anticipated that the brush layer thickness is $\sim Na\sigma$.

The regimes of behaviour of the brush layer thickness are;

(i) $0 < \sigma \leq N^{-6/5}$.

Swollen Mushroom; $P < N^{1/2}$

$$h \sim N^{3/5} a P^{-1/5} \quad (1)$$

Ideal Mushroom; $P > N^{1/2}$

$$h \sim N^{1/2} a. \quad (2)$$

(ii) $N^{-6/5} < \sigma < 1$:

Stretched wet brush $P < N^{1/2}$

$$h \sim NaP^{-1/3} \sigma^{1/3} \quad (3)$$

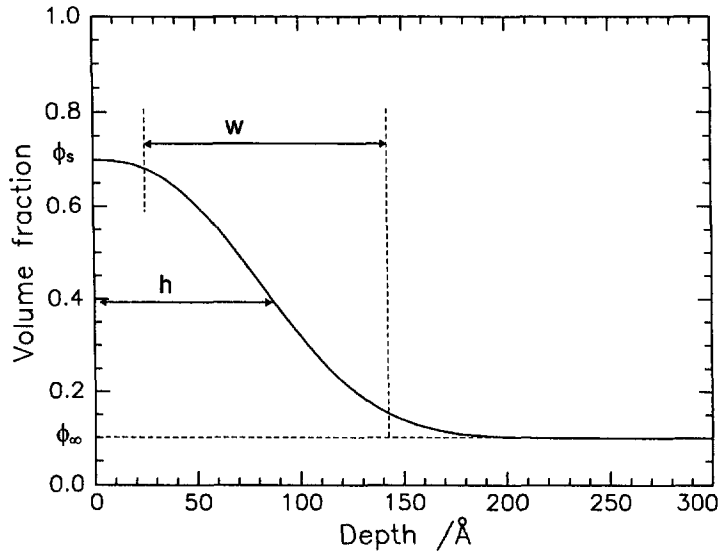


Fig. 1. — Schematic volume fraction profile for a polymer brush layer at a surface. Surface excess, z^* , is the area between the curve and the horizontal dashed line indicating bulk volume fraction. Surface and equilibrium bulk volume fractions, ϕ_s and ϕ_∞ respectively, are shown together with the width, w , and height, h , of the brush.

(iii) $N^{-1} \leq \sigma \leq N^{-1/2}$, $P > N^{1/2}$.
Unstretched brush layer

$$h \sim N^{1/2} a. \quad (4)$$

(iv) $N^{-1/2} \leq \sigma \leq 1$, $P > N^{1/2}$.
Stretched dry brush

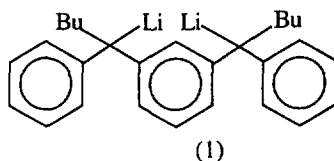
$$h \sim Na\sigma. \quad (5)$$

The self consistent field theory description of grafted polymers in polymeric matrices has been discussed in detail and the results of model calculations set out by Shull [12]. A major factor is that although matrix molecules are expelled from the grafted layer in the dry brush regime, complete expulsion is not expected because the resultant concentration gradient invokes too high a free energy penalty. This deformation of matrix molecules is accounted for in minimising the free energy to produce a volume fraction profile of the grafted polymer. A notable result from the self consistent field theory for polymers wherein the driving force for attachment is large and for $P > N$, is that the volume fraction profiles are describable (*i.e.* the shape and the extent of stretching in the brush) by the ratio z^*/R_g , where z^* is the surface excess of the grafted polymer and R_g the unperturbed radius of gyration.

At this point it is opportune to define the parameters of note for a brush like layer. Figure 1 shows a schematic volume fraction profile and marked on it are the surface volume fraction, ϕ_s , the equilibrium volume fraction, ϕ_∞ , and the surface excess. Also shown are two frequently reported parameters, the brush height, h , and the width, w , of the interface between grafted chains and matrix polymer. The normalised grafting density, σ , is given by z^*/Na and the average volume fraction of grafted polymer in the brush is z^*/h .

Experimental

POLYMERS. — Deuterio polystyrene was synthesised by anionic polymerisation in benzene under high vacuum conditions. The initiator used was 1,3 phenylene bis (3-methyl-1-phenyl pentylidene) dilithium (1):



which produces a difunctional polystyryl anion. On complete consumption of the monomer the living anions were "killed" by the addition of an excess of 1H, 1H, 2H, 2H-perfluorooctyl dimethyl chlorosilane. The fluorosilane terminated polymer so obtained (DPSF2) was isolated by precipitation in methanol followed by redissolution and reprecipitation a further two times. This procedure has been shown to remove any unreacted fluorosilane terminating agent from the polymer. Figure 2 shows in schematic form the nature of this polymer. A perdeuteropolystyrene of similar molecular weight (DPS) was also prepared but terminated normally by addition of methanol, *i.e.* the polymer was unfunctionalised at its ends.

Hydrogenous polystyrenes with a range of molecular weights were obtained from Polymer Laboratories (Shawbury, Shropshire, UK) and used as received. The molecular weights and molecular weight polydispersities obtained from size exclusion chromatography of all polymers used are given in Table I.

NEUTRON REFLECTOMETRY. — DPSF2 was mixed with each of the hydrogenous polystyrenes in varying proportions and dissolved in toluene to give solutions *circa* 2% (w/v) of total polymer content. Thin films of the mixed polystyrenes were spun cast by depositing small volumes of each solution on to the polished surface of a silicon block (thickness 0.5 cm, diameter 5 cm) spinning at 2000 rpm. The native oxide layer was not removed from the silicon but each block had been previously cleaned by ultrasonication in a warm toluene bath and dried under vacuum. After spin casting, each block was placed in a vacuum oven and the polymer film annealed at 413 K for 6 days. To prevent de-wetting during this annealing, somewhat thicker films of the mixtures with the lowest molecular weight hydrogenous polymer were prepared. Separate ion beam analysis experiments and ATR FTIR work showed that the annealing time of 6 days was more than sufficient to ensure that the equilibrium conditions were obtained.

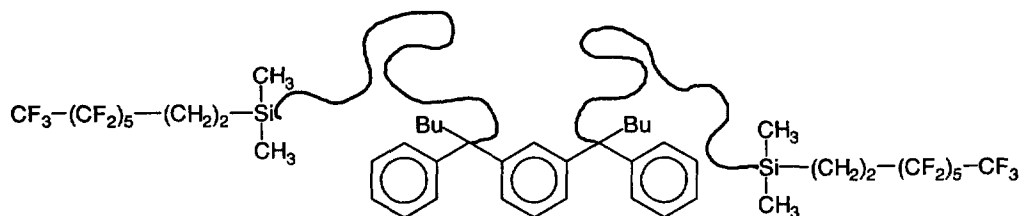


Fig. 2. — Chemical features of DPSF2 polymer.

Table I. — *Molar masses and polydispersity of polymers.*

Polymer	$\bar{M}_w/10^3$	\bar{M}_w/\bar{M}_n
DPSF2	98.4	1.04
DPS	106	1.06
PSH 52K	52	1.03
PSH 100K	106	1.06
PSH 330K	330	1.04
PSH 1M	1075	1.05

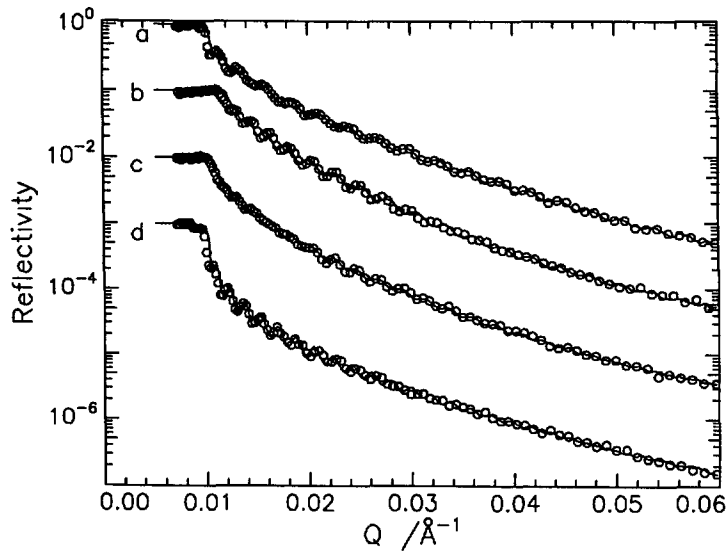


Fig. 3. — Typical reflectivity profiles and the fit (solid line) of calculated reflectivity from the functional form models. a) 10% DPSF2 in 1M PSH matrix; b) 5% DPSF2 in 100 K PSH matrix; c) 20% DPSF2 in 52 K PSH matrix; d) 30% DPSF2 in 330 K matrix. Profiles are shifted down 1 decade in reflectivity from preceding profile for b), c) and d).

Neutron reflectometry profiles were obtained using the SURF reflectometer located on the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, Chilton, Oxon, UK. The wavelength range of the incident neutron beam was $0.5 \leq \lambda/\text{\AA} \leq 6.5$ and three angles of glancing incidence on the sample were used (0.21° , 0.5° and 1.35°), the range of momentum transfer, Q , thus covered was from ~ 0.007 to 0.14 \AA^{-1} . A single time of flight detector was used and the specularly reflected neutron intensities from each of the different geometries were combined and placed on an absolute scale by setting the region at low Q , where total reflection was evident to a reflectivity of 1. The background due to incoherent scattering was calculated from the reflectivity over the Q range 0.06 \AA^{-1} to 0.14 \AA^{-1} . This was subtracted from the combined reflectivity data to give reflectivity profiles on an absolute scale.

Results

Typical reflectivity profiles are shown in Figure 3, a number of fringes are evident arising mainly from the total thickness of the polymer film on the silicon block. Additionally, close inspection of the reflectivity in the region of the critical edge for those specimens with the higher volume fractions of low molecular weight hydrogenous polystyrenes reveals a step in the reflectivity profile. This is due to a reduction in the reflected neutron intensity due to incoherent scattering and similar reflectivity profiles have been observed in other polymer systems. Because of this effect, in analysing the neutron reflectivity data we have used the complex scattering length density in calculating the reflectivity from model functions. To calculate the reflectivity, the volume fraction profile at the surface was divided into a number of laminar layers and the neutron refractive index, n , calculated for each layer;

$$n = 1 - \frac{\lambda^2}{2\pi} \rho_n + i \frac{\lambda \rho N_A (\sigma_i + \sigma_A)}{m 4\pi} \quad (6)$$

Where ρ_n is the scattering length density of the layer, m the scattering unit molar mass, ρ the physical density of the polymer and σ_i and σ_A are the incoherent scattering and absorption cross sections of the layer species. For ^1H nuclei, σ_i is considerably wavelength dependant, however, $(\sigma_i + \sigma_A)/\lambda$ generally does not deviate markedly from an average value, and for ^1H over the range $2 < \lambda/\text{\AA} < 5$ this ratio is 10.3 ± 3 barns/ \AA , consequently equation (6) can be rearranged in terms of $(\sigma_i + \sigma_A)/\lambda$ and the average values used.

Volume fraction near surface depth profiles were modelled using two functions; an error function profile which along with tanh profiles has been used to describe stretched dry brush layers and has some foundation on self consistent field theory

$$\phi(z) = \frac{(\phi_s - \phi_\infty)}{2} \left[1 + \operatorname{erf} \left(\frac{z - h}{w} \right) \right] + \phi_\infty \quad (7)$$

and an expanded exponential profile

$$\phi(z) = (\phi_s - \phi_\infty) \left[\exp \left(- \left(\frac{z}{\lambda} \right)^\alpha \right) \right] + \phi_\infty \quad (8)$$

In the expanded exponential function, λ is the characteristic decay length descriptive of the distance over which the volume fraction falls from that at the surface, ϕ_s , to the bulk volume fraction, ϕ_∞ , of DPSF2. Of the two functional forms the expanded exponential is the more flexible since the value of the exponent α can change the character of the volume fraction profile from simple exponential ($\alpha = 1$), through Gaussian ($\alpha = 2$), to a rectangular slab (α large) and encompasses the error function profile between $\alpha = 2$ to α large. Moreover we note that Gaussian profiles have been proposed for polymers with loop configurations at surfaces [37]. Such configurations may be evident here because of the functionalisation of both ends. Parameters of each of the functional forms were obtained by recursively fitting the reflectivities calculated using these equations to the data. In outline, initial values of the parameters (ϕ_s , ϕ_∞ , λ , α etc.) were provided and the near surface depth profile calculated using the appropriate equation. The profile was then divided into laminar strips of 10 \AA thickness and the neutron refractive index calculated for each of these strips using the volume fraction composition and the known scattering length densities and cross sections of DPSF2 and PSH. The reflectivity of this assembly of layers was then calculated using the exact optical matrix method, incorporating roughness at the air-polymer and polymer-silicon substrate interfaces. This process was iterated until the change in reduced chi squared criterion of goodness of fit was within the specified tolerance between successive iterations. In general the value of the

Table II. — *Parameters of volume fraction profiles for DPSF2 and DPS mixtures.*

	ϕ_∞	ϕ_s	$z^*/\text{\AA}$	$\lambda/\text{\AA}$	α	$h/\text{\AA}$
PSH 1M Matrix	0.04 ₉	0.51	33	81	2.3	70
	0.09 ₆	0.86	56	84	2.0	69
	0.15	0.91	72	109	2.2	91
	0.29 ₇	0.96	74	125	2.3	107
PSH 330 K Matrix	0.04 ₉	0.45	26	73	2.1	62
	0.06	0.61	42	86	1.9	72
	0.15	0.84	63	104	1.9	85
	0.29 ₉	0.96	64	109	1.9	90
PSH 100 K Matrix	0.05	0.37	20	73	1.9	61
	0.08	0.47	29	84	1.98	68
	0.16 ₅	0.71	48	99	1.8	80
	0.24	0.83	54	103	1.9	84
PSH 52 K Matrix	0.05	0.34	19	74	1.9	61
	0.09 ₇	0.43	25	84	2.2	71
	0.15	0.60	38	95	1.6	76
	0.26	0.76	40	88	1.5	70
DPS Mixtures						
PSH 1M	0.17	0.27	9	99	2.6	
PSH 330 K	0.17	0.29	10	92	2	
PSH 100 K	0.17	0.26	8	107	2.4	

reduced chi squared [38] at the end of fitting was *circa* 4. Examples of typical fits from the use of either model function to the data are shown in Figure 3. Both equations (7 and 8) produced identical volume fraction profiles for any one reflectometry profile.

Because of the additional flexibility of the expanded exponential form, the values of z^* , ϕ_s *etc.* reported are solely from this functional form but we stress that they are identical for both functional forms used. Table II sets out the values of ϕ_s , ϕ_∞ , λ and α obtained for all mixtures of DPSF2 and PSH examined. Included in Table 2 are the surface excess, z^* , and the height of the brush layer, h . The surface excess is defined as;

$$z^* = \int_0^\infty (\phi(z) - \phi_\infty) dz. \quad (9)$$

Figure 4 shows typical volume fraction profiles obtained.

Before proceeding further, it should be established that the adsorption at the surface of DPSF2 exceeds that of the equivalent deuterated polymer without fluorosilane end groups. It is known that mixtures of deuterated and hydrogenous polystyrene have a surface which is enriched in deuteropolystyrene when the molecular weights of the two polymers are sufficiently high and the mixture is annealed at a temperature sufficiently close to the co-existence curve [39, 40]. On the basis of the molecular weight of the DPSF2 and the relatively low annealing temperature it was anticipated that surface segregation in the absence of fluorosilane

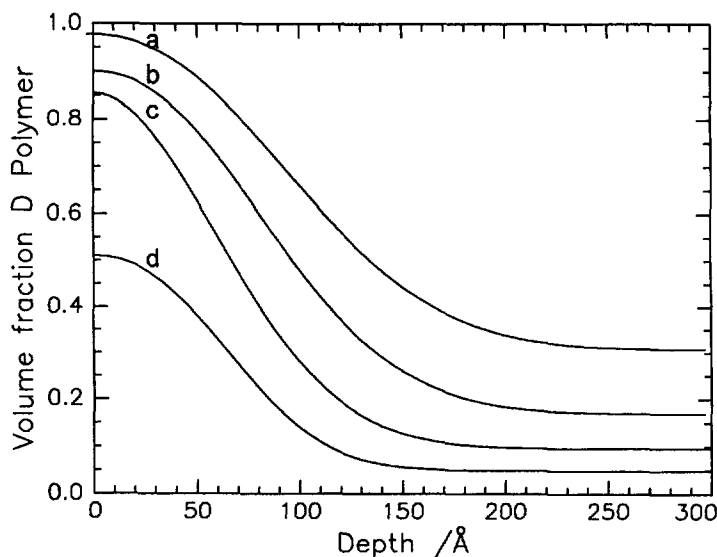


Fig. 4. — Volume fraction profiles obtained from fitting to neutron reflectometry data for DPSF2 in PSH of relative molar mass 1.075 M. ϕ_{∞} values are a) 0.297 b) 0.15 c) 0.09 d) 0.049.

groups should be small. Mixtures of DPS in the three highest molecular weight PSH polymers were made, the DPS content being *circa* 20% w/w. The mixture with the highest probability of surface segregation being evident was that where the matrix molecular weight was 1.075 M and the volume fraction profiles obtained are compared in Figure 5 to those for DPSF2 containing mixtures at approximately the same average composition. Evidently, DPSF2 is adsorbed to a significantly higher extent and this can only be attributable to the fluorosilane end groups and we conclude that the polymer is attached by its ends to the air-polymer interface. Furthermore, earlier SIMS and XPS experiments [41] on a polymer functionalised at one end only clearly show that there is an excess concentration of fluorine atoms at the surface.

The adsorption isotherms ($z^* f(\phi_{\infty})$) in Figure 6 have a marked molecular weight dependence, although in all cases the general behaviour is the same, *i.e.* an initial increase in z^* which rapidly approaches a plateau value. This behaviour is predicted by self consistent field theory, see below. Somewhat similar behaviour is shown for the dependence of ϕ_s on ϕ_{∞} (Fig. 7). Although there is no evidence of a plateau value being approached for these data, a marked dependence on the molecular weight of the PSH matrix is also evident and again this behaviour is predicted by self consistent field theory which we discuss more fully below.

Discussion

For a particular molecular weight matrix the volume fraction profiles show the same general qualitative shape as the equilibrium volume fraction increases (Fig. 4). Similarly, when approximately equal equilibrium concentration of DPSF2 is present in each of the PSH matrices, the profiles again have the same characteristics (Fig. 5). However, when volume fraction profiles for the similar surface excess values are compared, that for DPSF2 in the lowest molar mass PSH matrix (52 K) is evidently different, Figure 8. Thus we may be in a regime where expulsion of the matrix polymer from the brush layer is not so strong and the nature of the brush layer

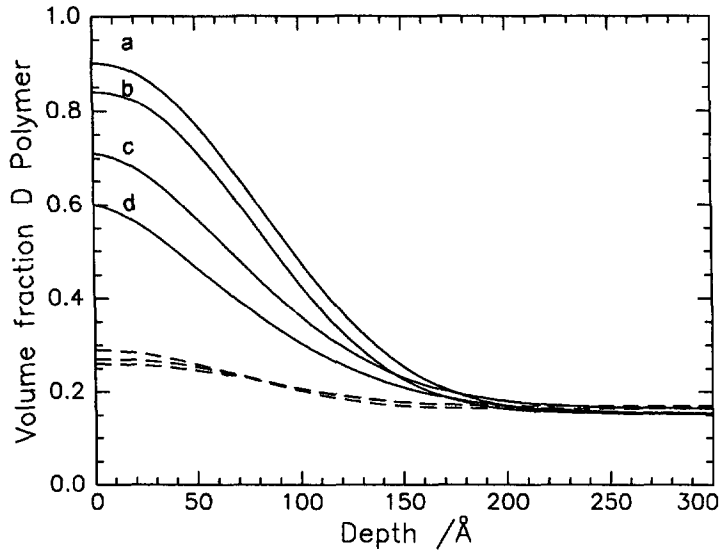


Fig. 5. — Volume fraction profiles of DPSF2 and unfunctionalised DPS at the same (approximately) equilibrium volume fraction. Relative molar masses of PSH matrices a) 1.075×10^6 , b) 330×10^3 , c) 106×10^3 , d) 52×10^3 . Dashed lines pertain to unfunctionalised DPS in PSH matrices of relative molar masses, 330×10^3 , 106×10^3 and 1.075×10^3 .

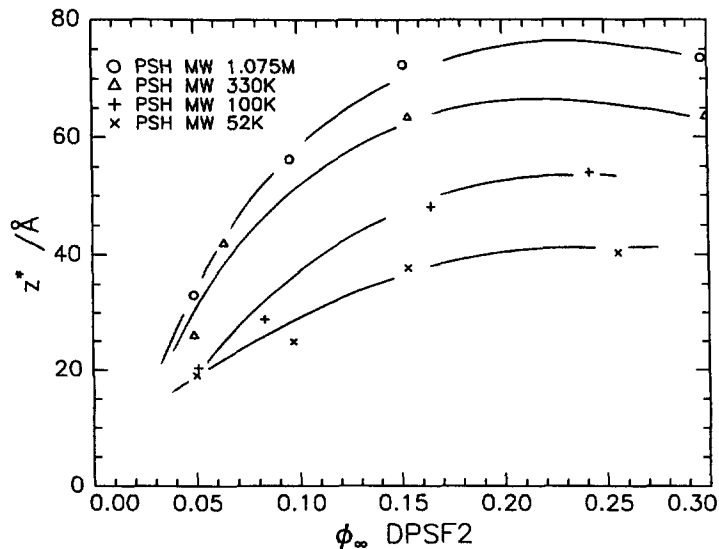


Fig. 6. — Surface excess of DPSF2 as a function of equilibrium volume fraction for each PSH matrix. Lines are guides to the eye.

may be in transition. From the values of z^* obtained and the degree of polymerisation of the DPSF2, the range of grafting density explored was $3 \times 10^{-3} \leq \sigma \leq 2 \times 10^{-2}$. The upper limit is an order of magnitude smaller than the highest value of $PN^{-3/2}$ attained (DPSF2 in the

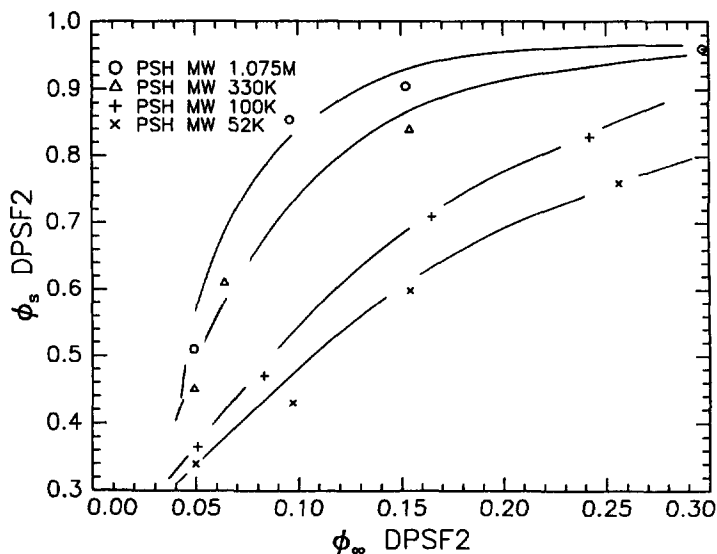


Fig. 7. — Surface volume fraction of DPSF2 as a function of equilibrium volume fraction in PSH matrix. Lines are guides to the eye.

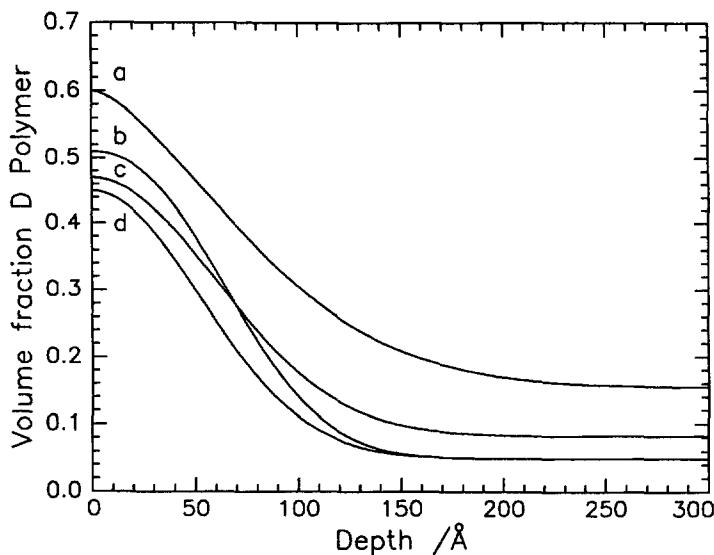


Fig. 8. — Volume fraction profiles in each PSH matrix at approximately the same value of z^* ($\sim 30 \pm 5/\text{Å}$) PSH matrix relative molar masses are a) 1.075×10^6 , b) 52×10^3 , c) 330×10^3 , d) 106×10^3 .

PSH matrix of molar mass 1.075×10^6) and although the lowest value of $PN^{-3/2}$ is 1.9×10^{-2} for the 52×10^3 molar mass matrix, the actual values of σ in this matrix were no larger than 7×10^{-3} . Hence at all times it appears that the grafted DPSF2 molecules should have ideal statistics. Furthermore the range of σ explored is in the range N^{-1} to $N^{-1/2}$ and given that

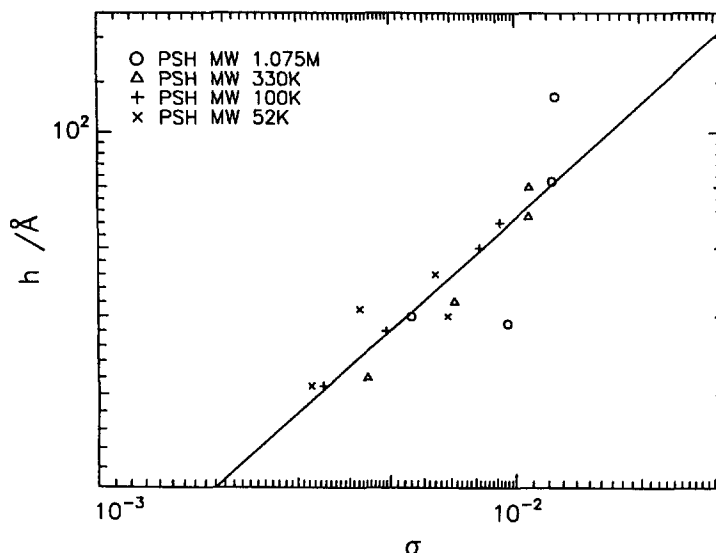


Fig. 9. — Brush height as a function of grafting density in all PSH matrices. Solid line is the linear least squares fit to all the data.

for all matrices $P \geq N^{1/2}$, then we anticipate unstretched brush characteristics for the surface layer. The grafting density values quoted above are calculated on the basis of only one end being located at the surface, however given that we have fluorosilane groups at each end then the grafting densities may be twice the range given above, *i.e.* $6 \times 10^{-3} \leq \sigma \leq 4 \times 10^{-2}$. Even with this correction the grafting densities still do not exceed the limits specified for unstretched brush layers. In contradiction to this expectation, it is abundantly evident that the brush height (h) is dependent on σ , Figure 9. The linear least squares line through all of these data gives a scaling relation

$$h \propto \sigma^{0.32} \quad (10)$$

The average volume fraction of DPSF2 in the layer and the DPSF2 surface volume fraction have a linear dependence on σ in the double logarithmic plot of Figure 10. Note that even for the highest molecular weight PSH matrix and for the highest concentration of DPSF2 in the mixture, the average volume fraction never reaches unity, the maximum is ~ 0.8 and hence complete expulsion of the matrix polymer from the adsorbed layer does not take place. For the average DPSF2 volume fraction the scaling relation observed is

$$\phi_{AV} \propto \sigma^{0.68 \pm 0.04} \quad (11)$$

Whereas for the surface volume fraction we have

$$\phi_s \propto \sigma^{0.78 \pm 0.04} \quad (12)$$

Since the excess polymer in the near surface profile expressed in volume fraction terms is given by:

$$z^* = h\phi_{AV}$$

and

$$\sigma = \frac{z^*}{Na},$$

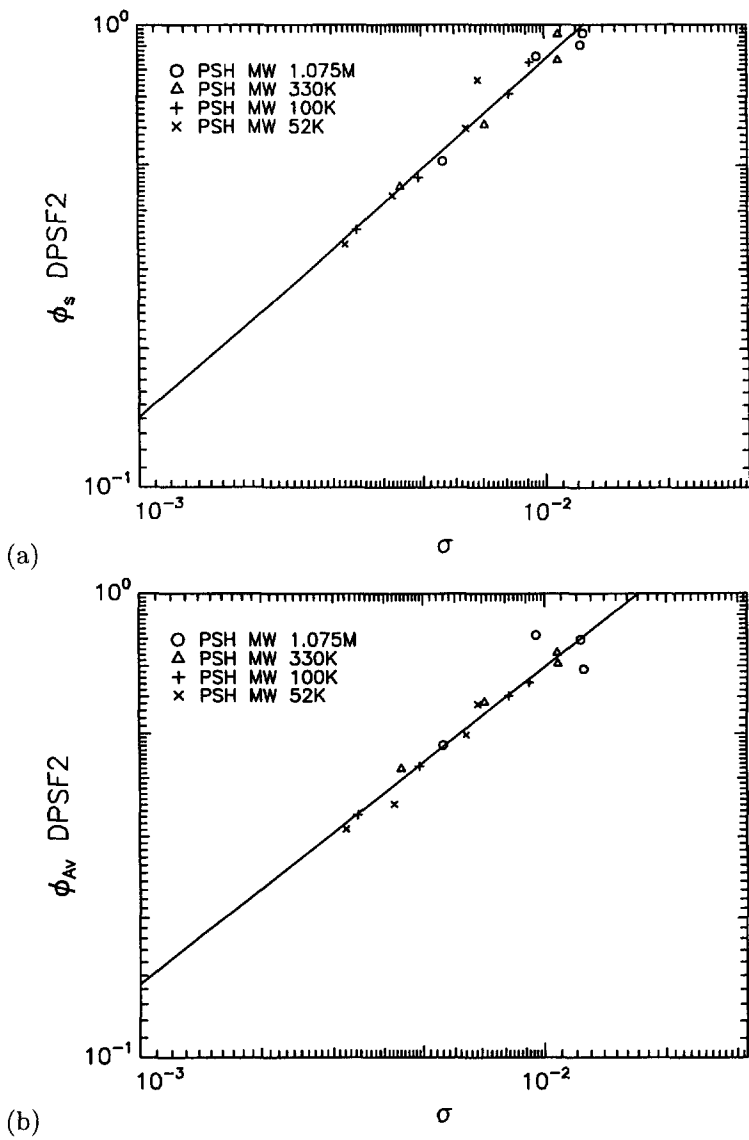


Fig. 10. — Surface volume fraction (a) and average brush layer volume fraction (b) as a function of grafting density. For both plots the solid line is the linear least squares fit to the data.

then

$$\phi_{AV} = \frac{Na\sigma}{h}$$

For the stretched wet brush regime, $h \propto \sigma^{1/3}$ (Eq. (3));

$$\phi_{AV} \propto \sigma^{2/3} \tag{13}$$

which agrees exactly with the scaling observed for the experimental data, equation (11). Our data do not display any dependence on P , the matrix molar mass, that we can discern with confidence.

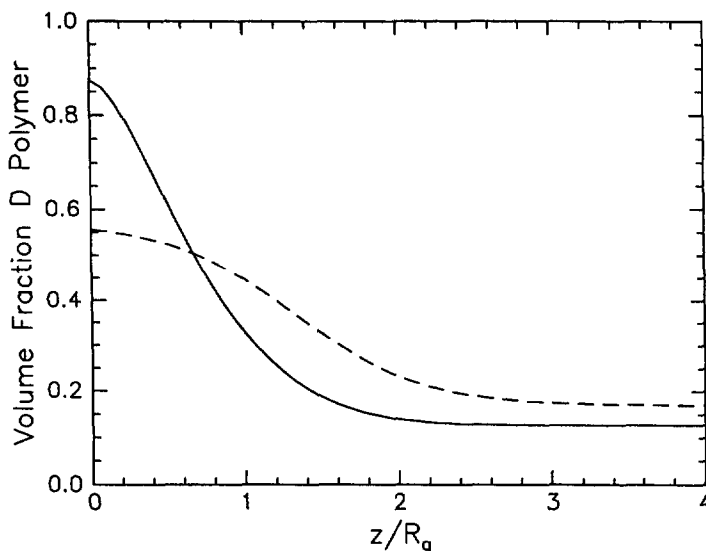


Fig. 11. — Volume fraction profiles obtained from neutron reflectometry for deuteropolystyrene functionalised at one end (- - -) and at both ends (solid line) blended with hydrogenous polystyrene under equilibrium conditions for equal normalised surface excess.

Self Consistent Field Analysis

A detailed description of the SCF theory for the dry brush, *i.e.* polymer brushes surrounded by matrix polymer of equal degree of polymerisation was first developed by Shull [12], more recently the treatment has been extended to situations where there is a transition from wet to dry brush characteristics [42]. It is appropriate at this point to establish the nature of the attachment of the DPSF2 to the air-polymer interface since although both ends of the polymer have an affinity for this interface there is no *a priori* reason why both should attach thus forming some sort of looped configuration. Shull has discussed the volume fraction profiles of polymers attached by one (tail configuration) or both ends and he demonstrates [43] that loop configurations produce a narrower profile than tail configurations. This comparison has to be made under conditions of equal normalised surface excess of polymer (z^*/R_g). In Figure 11 we plot volume fraction profiles for DPSF2 in PS and for a mixture containing deuteropolystyrene with the same fluoro silane group at one end only. For both cases the normalised surface excess is ~ 0.56 . Clearly the volume fraction profile for the DPSF2 containing blend is much narrower than that for the single end functionalised polymer and thus the dominant configurations of the DPSF2 molecules are those with both ends at the air-polymer interface. We acknowledge that there is a small probability that some of the adsorption is due to DPS segments in the middle of the molecule as indicated by the volume fraction profiles in Figure 5 and the z^* values in Table II for unfunctionalised DPS. However the values of z^* for unfunctionalised polymer are 6 to 10 times smaller than those for DPSF2 and their contribution to the total adsorption must be small. Because of this all subsequent discussion using the SCF analysis is explicitly for polymer with an adsorbing moiety at each end with both of them being located at the air - polymer interface. An important quantity is the adsorption parameter, β , defined so that $k_B T \beta$ is the net free energy decrease when the adsorbing end is confined to the first lattice of the surface region. This adsorption parameter is related to the difference between

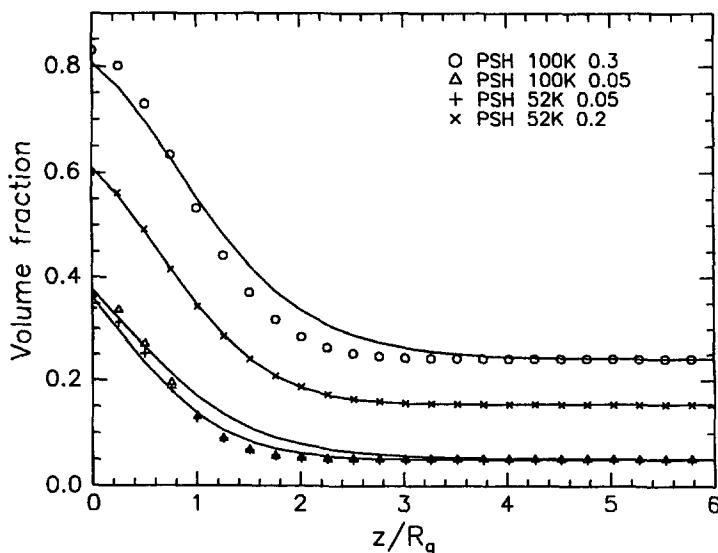


Fig. 12. — Fit of self consistent field theory calculated volume fraction profile (line) to experimental data for two PSH matrices. Relative molar mass of each matrix and the volume fraction of DPSF2 in each is noted.

the interaction parameter of the functionalised end with the surface (χ_e^s) and with the bulk (χ_e^b) such that;

$$\beta = (\chi_e^b - \chi_e^s) + 1.1 \ln(a/R_g). \quad (14)$$

Equation (14) was originally derived for polymer molecules with one sticky end, and not withstanding the fact that the confinement term will be different for polymers with two sticky ends, this equation is applicable without alteration to the polymers being discussed here [44]. Within the SCF theory, $(\chi_e^b - \chi_e^s)$ is adjustable and exhibits significant control on the form of the volume fraction profile normal to the surface or interface. Volume fraction profiles calculated by the SCF theory for polymers with two sticky ends were non-linearly least squares fitted to the experimentally obtained profiles by adjusting $(\chi_e^b - \chi_e^s)$. Typical fits are shown in Figure 12 and the average value of $(\chi_e^b - \chi_e^s)$ which resulted for the DPSF2 degree of polymerisation was 3.8 ± 0.1 and the value of β which results is *circa* 1.05. Figure 12 exhibits the same characteristics which have been observed for other systems, *i.e.* the SCF profile generally crosses the curve of the experimental points and is usually somewhat broader than the experimental volume fraction profile. The surface volume fraction obtained from the SCF calculation is in good agreement with the data. Clarke [17] suggested that the broadening of the SCF curves was due to a combination of using average chain statistics and the large perturbation of the real chain statistics by the surface to which polymers were adsorbed. A further confirmation of looped configurations of DPSF2 dominating is shown in Figures 13 where the results of attempting to fit the experimental volume fraction profiles with both one and two end functionalised solutions to the SCF equations are shown. Clearly the single end fits are considerably worse than those for a molecule attached by both ends. Figure 14 shows a comparison of the surface volume fraction of DPSF2 obtained from the reflectometry data compared with the SCF theory calculated values and the two sets of values are qualitatively in agreement in their variation with ϕ and their magnitude although absolute agreement is not obtained. These comments also apply

to the comparison of normalised surface excess values as Figure 15 shows, the disparity between experimental and self consistent field calculated values of z^*/R_g becoming greater with increasing matrix molecular weight. We remarked earlier that the calculated and experimental profiles are very similar in their behaviour to that observed by Clarke *et al.* [17] for carboxylic acid terminated polystyrene grafted to the native oxide layer of silicon. However, no comparisons with surface excess values from SCF theory were made, and consequently we cannot say whether the trend observed here is unique to polymers with both ends functionalised or symptomatic of failures in the self consistent field approach due to increased configurational distortion in the PSH matrices of higher molecular weight. It could be argued that the self consistent field calculation is inappropriate for the DPSF2 molecule used here, and that more relevant models may exist. In a recent comparison of SIMS and neutron reflectivity data for carboxylic acid terminated polystyrene and linear di and triblock copolymers of vinyl pyridine and polystyrene, Liu *et al.* [21] compared many different models and concluded that no one model produced profiles which were in markedly better agreement with data than any other model. However what their results do show is the screening of excluded volume interactions in the bulk melt is equally operational in the region of a perturbing boundary such as a wall or surface.

A possibility is that the relatively large fluorosilane groups aggregate in the surface plane. In this case we could have regions of much higher local grafting density, σ , than the average values calculated above and some regions where σ is much lower. As a consequence the average brush height may be somewhere between that for a stretched dry brush and an undeformed brush, leading to the apparent behaviour as a stretched wet brush. In rebuttal of this point it can be said that the fluorosilane groups are less bulky than some of the short blocks used as anchors in other studies of brush behaviour [21]. Moreover, in separate small angle neutron scattering experiments on mixtures of DPSF2 and PSH we have seen no evidence of micelle formation, the radius of gyration was that of unperturbed polystyrene over the composition range $5 \leq c/(\%w/w) \leq 20$. Consequently, we are of the opinion that surface aggregation of fluorinated groups is negligible.

The dependence of the brush height on σ is unexpected and regrettably there are few other such comparisons reported in the literature. Klein *et al.* [45] used NRA to determine brush heights in matrix molecular weights of 9000 and 330 000. In the lower molecular weight matrix a σ exponent of 0.33 was obtained as anticipated because the brush was swollen by the lower molecular weight matrix. For the higher molecular weight matrix an exponent of 0.54 was obtained which was interpreted as being due to the brush being in a transition region from the screened non swollen region (where there is no dependence of h on σ) to the stretched dry brush ($h \sim \sigma$). From values of h and σ reported by Kramer *et al.* [15], for a polystyrene (molecular weight 250 000) end capped with a few segments of polybutadiene surrounded by a PSH matrix with a molecular weight of 575 000 an exponent of 0.6 was obtained, significantly different from either the screened or stretched brush cases. One point that may be germane is that although the values of h in Table II are $\approx R_g$ of DPSF2, because of the dominant loop configurations the relevant R_g value should be that of polymer molecules with a degree of polymerisation of $N/2$ attached by one end. In this case the R_g is *circa* 60 Å and thus $h \approx 3R_g/2$ in Table II.

Very recently Shull [42] has extended the SCF calculation to the crossover region between high and low molecular weight matrices and distinctive relations for the normalised surface excess (z^*/R_g) are obtained for the wet brush and dry brush regimes. For wet brush regime

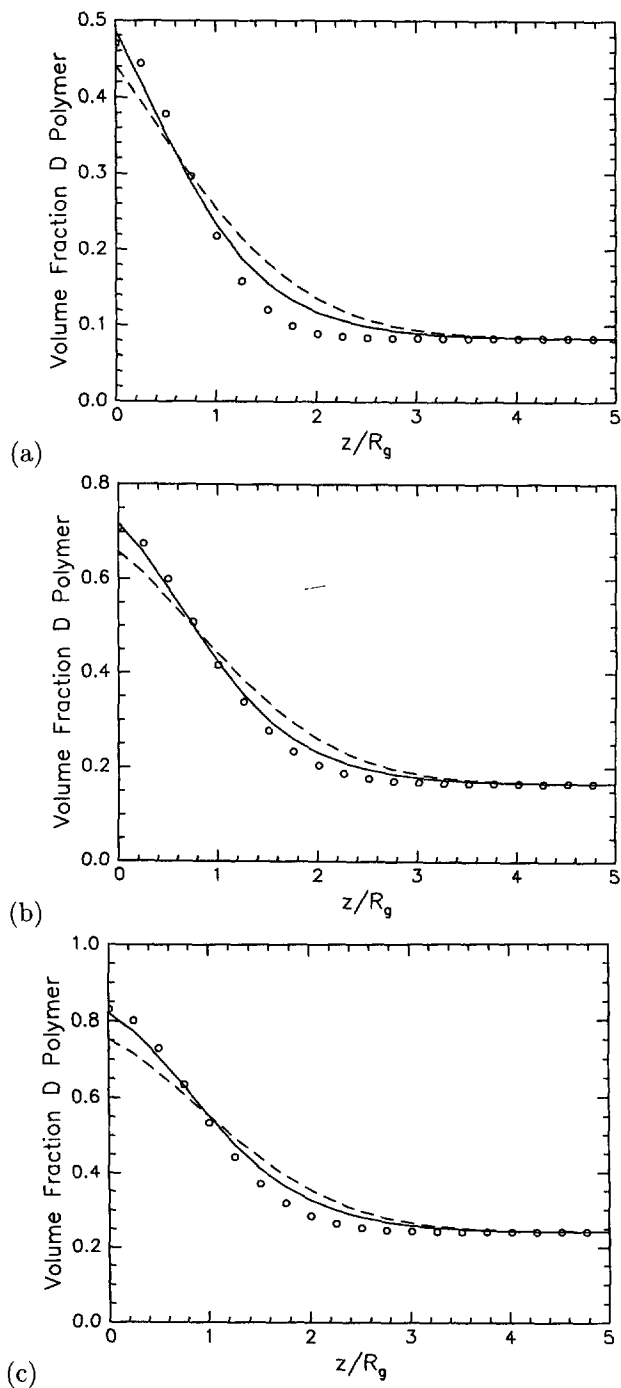


Fig. 13. — Attempted fit of SCF equations for polymers with one (- - -) and two (solid line) “sticky” ends to the volume fraction profiles obtained for DPSF2 in a hydrogenous polystyrene matrix of molar mass 106×10^3 . Equilibrium bulk volume fractions of DPSF2 are a) 0.08; b) 0.165; c) 0.24.

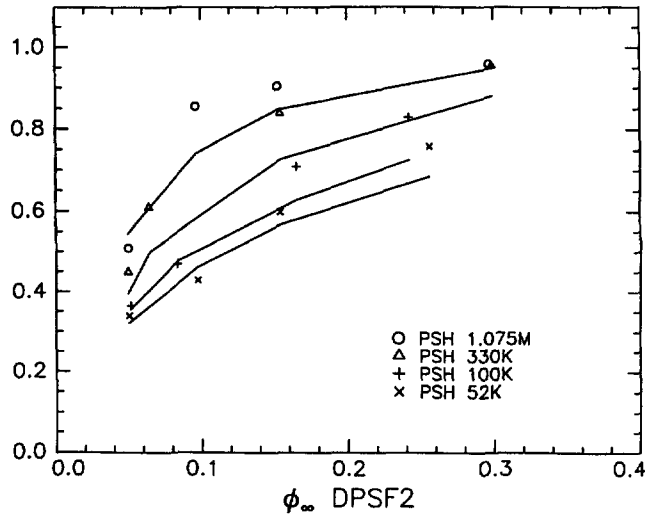


Fig. 14. — Experimental values of surface volume fraction of DPSF2 compared with those calculated (solid lines) using self consistent field theory with a sticking energy of $1.05 k_B T$.

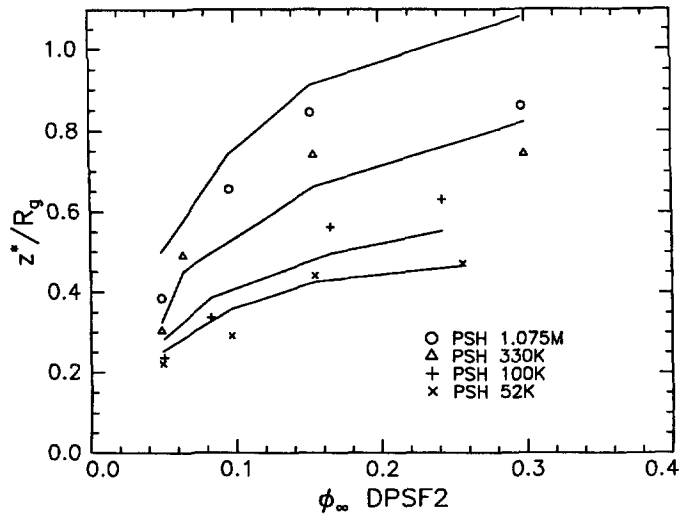


Fig. 15. — Normalised surface excess (z^*/R_g) from self consistent field theory (solid line) compared to experimental values.

with $\chi P \ll 0.5$, where χ is the interaction parameter between brush polymer and matrix polymer

$$z^*/R_g \propto (\ln \phi_\infty + \beta)^{3/2} \tag{15}$$

when $\chi P = 0.5$

$$z^*/R_g \propto (\ln \phi_\infty + \beta) \tag{16}$$

and in the dry brush regime

$$z^*/R_g \propto (\ln \phi_\infty + \beta)^{1/2} \tag{17}$$

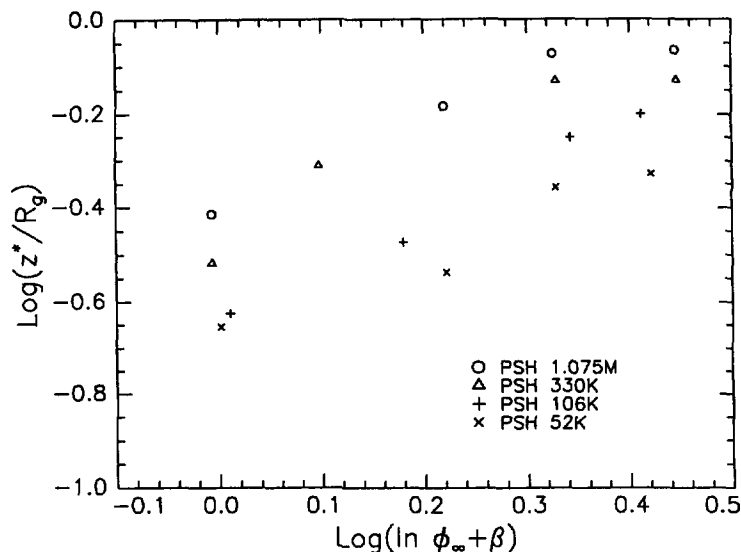


Fig. 16. — Double logarithmic plot of normalised surface excess on $\ln \phi_\infty + \beta$ for each PSH matrix.

Values of z^*/R_g obtained from the experimental volume fraction profiles are plotted as a function of $\ln \phi_\infty + \beta$ in the double logarithmic plot shown in Figure 16. The data sets form four approximately parallel sets the slopes of which from individual least squares fitting are 0.9 ± 0.10 . This appears to place the brush in the wet regime but with $\chi P = 0.5$, a value which does not concur with the scaling relation for the brush height and grafting density noted earlier. We remark at this point that no matter how the thickness of the adsorbed layer is calculated (*e.g.* the ellipsometric thickness, or the second moment of the volume fraction distribution), all lengths scale with σ with some exponent of *circa* 0.3. A possible cause of the observations noted for the doubly end functionalised polymer is that the chain statistics are perturbed by the polymer surface to a greater extent than for single end functionalised polymers. This enhanced perturbation also increases the distortion of the matrix molecules in their efforts to fill space and the net result is that the brush layer has hybrid characteristics.

Conclusions

Functionalising polystyrene at each end of the molecule with a low surface energy fluorosilane, produces a greatly enhanced adsorption of the polymer at the air-polymer interface when it is mixed with hydrogenous polystyrene. The parameters of the volume fraction profile obtained from neutron reflectometry data for annealed thin films have been compared with scaling law relations and self consistent field calculations. A hybrid character is displayed by the brush layer; the brush height or layer thickness scales with grafting density in a manner predicted for a stretched wet brush. Effects of the matrix molecular weight on surface excess and equilibrium surface volume fraction are evident. In the case of the surface volume fractions, these values can be well reproduced using a sticking energy of $1.05k_B T$ for the fluorosilane attaching to the air surface. However, the self consistent field theory does not reproduce the adsorption isotherm so well, the discrepancy with experimental values becoming more evident as the matrix molecular weight increases. Further evidence of the hybrid nature of the surface brush layer has been

obtained by noting the dependence of the normalised surface excess on $\ln \phi_{\infty} + \beta$. Behaviour corresponding to a wet brush with $\chi P = 0.5$ is observed which contradicts the scaling of brush thickness with grafting density.

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