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The Structure of Grafted Polystyrene Layers in a Range of Matrix Polymers

C. J. Clarke* and R. A. L. Jones

Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.

J. L. Edwards

ICI Colloid Science Group, The Heath, Runcorn, Cheshire WA7 4QE, U.K.

K. R. Shull

Department of Materials Science and Engineering, 2225 North Campus Drive, Evanston, Illinois 60208-3108

J. Penfold

Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, U.K.

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ABSTRACT: We have used neutron reflectivity to measure concentration profiles of brushes of grafted chains in the melt. A method has been developed for permanently grafting end-functionalized polymers to a silicon substrate. By changing the matrix polymer surrounding the brush, we have investigated how the conformation of the brush depends upon the interaction between the matrix and brush polymers. We have observed strong stretching of the brush chains when the matrix and brush interact favorably, and collapse of the brush onto the substrate when they are immiscible. Comparisons have been made with theoretical predictions for the height and width of the brush, and experimental profiles have been compared with numerical self-consistent field theory.

Introduction

In many composite and multiphase 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, fracture, or chemical reaction. These processes have been extensively investigated at surfaces, but it is significantly more difficult to study buried interfaces nondestructively due to their inherent inaccessibility. There has been much interest in recent years in developing an improved understanding of the nature of interfaces at the molecular level. One system which has been the subject of both experimental[1-3] and theoretical[4-6] studies consists of polymer layers which are attached by one end to a surface. These systems (sometimes known as brushes) are of considerable importance because of their potential applications in composite materials, adhesives, lubricants, and colloidal stabilizers among others. Typically, the polymer is grafted to the surface by a short block of adsorbing copolymer or by a functional group which exhibits an affinity for the surface. Almost all previous experimental work in this area has been on systems where the bond is physical rather than chemical in nature. This has the consequence that polymers which have attached to the surface may be able to remove or rearrange themselves. Much of the theoretical work in this area however assumes that the surfacce coverage is fixed. Furthermore, it is difficult to produce a brush of one polymer in a matrix of a different polymer. For example, block copolymers form brushes at the interface between immiscible homopolymers with each block in its homopolymer phase. It is of great importance therefore to be able to reliably graft polymers onto a substrate via a permanent covalent bond. We have developed a process for doing this.

Numerical solutions of the self-consistent field (SCF) equations for grafted polymer layers have recently been reported.[7] Self-consistent field theory relies on the mean field approach,[8] 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 determining the conformation of chains attached to a surface in a range of matrix polymers, it is possible to test these calculations. Neutron reflectivity (NR) is an ideal technique for this investigation since the contrast in neutron scattering lengths between hydrogen and deuterium gives high depth resolution (~5 Å). This allows the detailed shape of the brush segment density profile to be determined and compared with SCF profiles.[9] It is also possible to test predictions of the height of the brush (the distance which it extends into the matrix polymer) and the interfacial width between the brush and the matrix.

Experimental Section

Monodispersed carboxy-terminated deuterated polystyrene, dPS(COOH), was obtained from Polymer Laboratories. It had been prepared by anionic polymerization, the living chains being terminated with solid carbon dioxide. This produced a yield of about 85% carboxy-terminated deuterated polystyrene. Carboxy-terminated deuterated polystyrene adsorbs to the native oxide layer on a silicon substrate via hydrogen bonds.[10] Triethoxysilane end groups are known to form covalent bonds with silanol groups in the native silicon oxide layer.[11] The carboxy-terminated polystyrene was modified by the reaction scheme shown in Figure 1 with the following experimental procedure.

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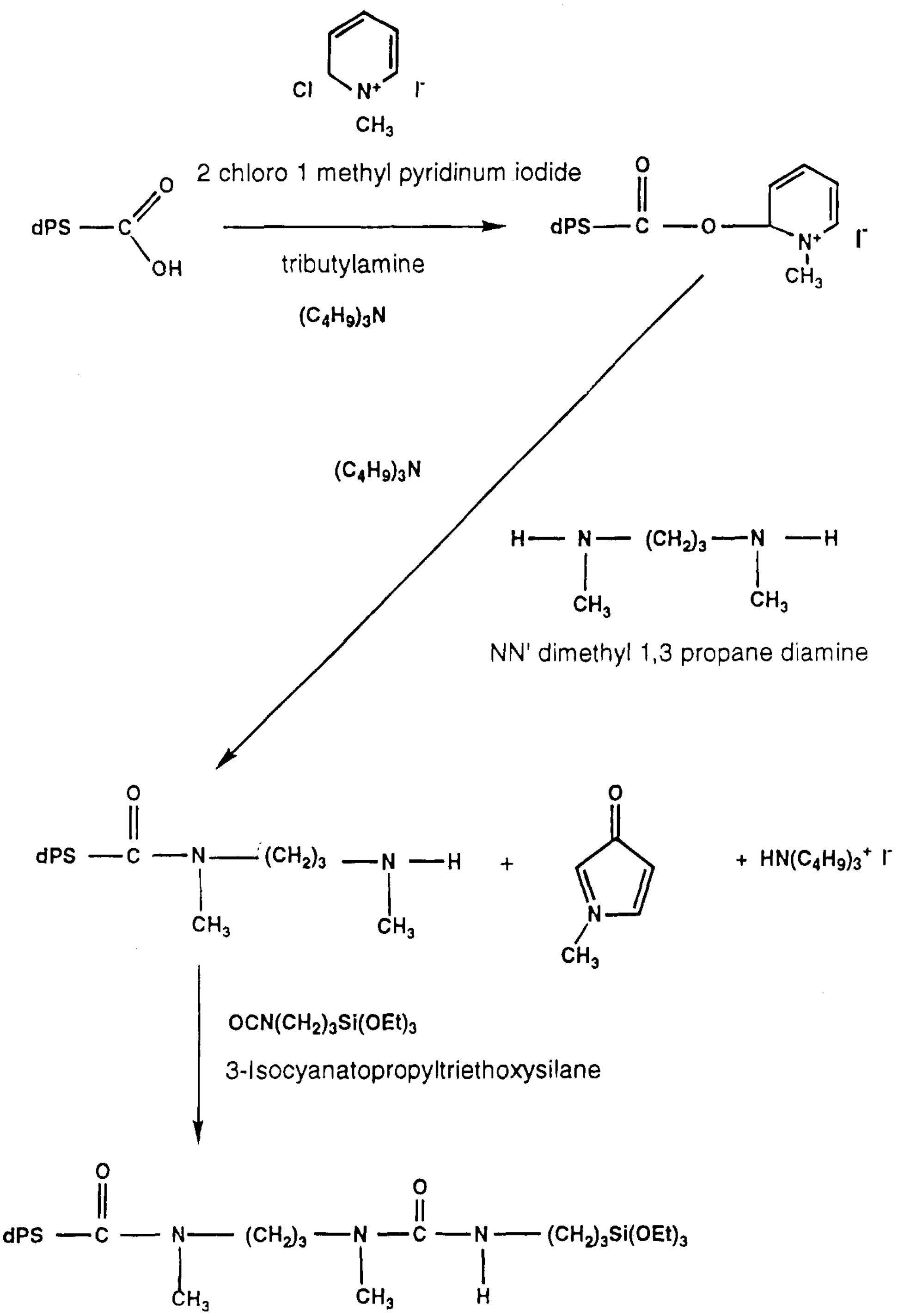

Figure 1. Reaction scheme used to convert the carboxy end group on deuterated polystyrene chains to a triethoxysilane group.

Stock solutions were prepared: 0.25 g 2-chloro-1-methylpyridinium iodide (CMPI), 0.5 mL of tributylamine, 0.5 mL of *N,N'*-dimethyl-1,3-propanediamine, and 1 mL of (3-isocyanatopropyl)triethoxysilane, each in 100 mL of dichloromethane. dPS(COOH) (0.25 g) was dissolved in dichloromethane in the reaction vessel. A 1 mL aliquot of each of the CMPI, tributylamine, and diamine solutions was then added (an excess), and the mixture was stirred and allowed to react overnight. Then 2 mL of the isocyanate solution was added (approximately a 2 times excess), and the mixture was left to react for a further 2 h. The modified polymer was then precipitated out with methanol and centrifuged. The supernatant liquid was removed and the precipitate was washed and redissolved in toluene.

Single crystal silicon wafers were cleaned with methanol and etched in oxygen plasma for 3 min to leave a uniform surface layer of silicon oxide, about 20–25 Å thick. The oxide layer was characterized by ellipsometry. The solution of modified polymer was spin coated onto the treated wafers to produce a layer of polymer ~300 Å thick. The coated wafers were annealed overnight in a vacuum oven at 184 °C, to enable the end groups to move to the substrate to form bonds. The polymer that had not grafted was then removed by gently wiping the surface with a lens cleaning tissue impregnated with toluene. The remaining layer was characterized by ellipsometry and was found to be ~70 Å thick. The thickness remained constant on further wiping. It was not always possible to produce films of exactly the same thickness after wiping, so there is some variation in the total amount of polymer grafted to the substrate. The bulk matrix polymers were then added by spin coating on top of the grafted layer to form a film ~3000 Å thick. After spinning, the films were annealed in a vacuum oven until equilibrium was reached. 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 analyzed by either a

Table 1. Characteristics of the Polymers Used in This Study

polymer	M_w	M_w/M_n	source	temp (°C)
dPS(COOH)	79 750	1.04	Polymer Labs	
PBD	10 000	1.06	L. J. Fetters	100
PBD	540 000	1.06	L. J. Fetters	120
PMMA	79 000	<1.09	Polymer Labs	184
hPS	500 800	1.06	Polymer Labs	184
hPS	156 000	1.03	Polymer Labs	184
hPS	52 000	1.03	Polymer Labs	184
hPS	28 500	1.03	Polymer Labs	184
hPS	7 000	1.04	Polymer Labs	184
PVME	99 000	2.13	Scientific Polymer Products Inc.	100
(PPO 50.6%)	244 000	7.63	Aldrich	184
(hPS 49.4%)	500 800	1.06	Polymer Labs	

simplex fitting routine or by using maximum entropy methods[12] to minimize the χ^2 parameter.

Five bulk matrix polymers were used: polybutadiene (PBD) and poly(methyl methacrylate) (PMMA) are immiscible with dPS; protonated polystyrene (hPS), has a very small interaction parameter with dPS and therefore behaves as a neutral matrix; poly(vinyl methyl ether) (PVME) and a 50–50 blend of hPS and poly(phenylene oxide) (PPO) interact favorably with dPS. It was necessary to use a blend to produce suitable films by spin coating. The polymer characteristics and annealing treatment are summarized in Table 1.

The annealing temperature was varied from 100 to 184 °C according to the glass transition temperature of the bulk polymer. Since the chains do not need to diffuse through the sample but only rearrange themselves at the interface, equilibrium should be reached fairly quickly. Since the matrix layer is added by spin coating, considerable mixing between the brush and the matrix can take place before the sample is annealed. To check that equilibrium has been reached, samples were annealed for several different lengths of time. For the polybutadiene matrix, samples were annealed for 10 min, 1 h, and 5 h. The interface width narrowed on annealing for 10 min and was narrower still after 1 h. After 5 h no further change in the profile was observed. The samples with a polystyrene matrix was annealed for 2 and 24 h, except for the lowest molecular weight where the film dewetted for the longer annealing times. Similarly, PVME samples were annealed for 5 min, 15 min, and 1 h. In each case, equilibrium was seen to be reached because the brush profile did not change on further annealing.

Results

Figure 2 shows reflectivity data, together with the best fits, for four of the matrix polymers used. Figure 3 shows the data and fits for three different molecular weight polystyrenes. For clarity, only data from a subset of the whole range of polymers listed in Table 1 are shown. The reflectivity varies dramatically, demonstrating that the conformation of the brush chains changes substantially with the matrix polymer. The reflectivity near the critical edge is particularly sensitive to changes in the brush profile because neutrons with 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 and thickness, so small changes in the brush profile can have a large effect on the reflectivity.

Equilibrium brush profiles (derived from the fits shown in Figure 2) for the five different matrix polymers are shown in Figure 4. The fits were 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 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, allowing for a layer of silicon oxide between the polymer and the substrate. The error function width, w, is related to the standard (Helfand) definition of the interface width a_I (from the gradient of the profile at the center of the interface), by[13]

$$a_I = \left(\left.\frac{\partial\phi}{\partial z}\right|_{z=h}\right)^{-1} = w\sqrt{\pi} \qquad (2)$$

Maximum entropy methods were used for the PVME data as no functional form (e.g. error function, exponential, or parabola) was found to match the data adequately. The fits had normalized values of χ^2 in the range 1.5–6.

Clearly the nature of the matrix has a great effect on the conformation of the brush. In the immiscible matrix polymer, the width of the interface between the brush and the bulk is narrow. As the brush and matrix polymers become more compatible, the brush chains begin to stretch out away from the substrate into the bulk, and solvent polymer begins to penetrate the brush. In the most miscible case, the chains extend up to 3 times their radius of gyration, and the volume fraction of matrix polymer within the brush reaches about 80%.

Discussion

Immiscible Matrix Polymers. For both 10k and 540k PBD, the interface between the brush and the matrix is narrow, 53 Å for both molecular weights. Genzer and Composto have measured the interfacial width between layers of PS and PBD homopolymers to be about 30 Å.[14] For PMMA, the equilibrium interfacial width was 84 Å. Again, this is larger than values of about 50 Å for homopolymer bilayers[15] or for diblock copolymers.[16,17] Unlike PBD however there is a substantial amount of PMMA within the brush.

Helfand and Tagami predicted that the interfacial width a_I between layers of two immiscible polymers, is given by

$$a_I = \frac{2a}{\sqrt{6\chi}} \qquad (3)$$

where a is the statistical segment length and χ is the interaction parameter.[18] This was modified to include polymers with different statistical step lengths by Helfand and Sapse[19] and later for finite molecular weights by Broseta et al.[20]

$$a_I = \frac{2}{\sqrt{6\chi}}\left(\frac{{a_A}^2 + {a_B}^2}{2}\right)^{1/2}\left[1 + \ln 2\left(\frac{1}{N_A\chi_{AB}} + \frac{1}{N_B\chi_{AB}}\right)\right] \qquad (4)$$

Using values of a = 6.7, 6.9, and 7.4 Å for PS, PBD, and PMMA, respectively, and $\chi_{\mathrm{dPS-PBD}} = 0.1$[21] and $\chi_{\mathrm{dPS-PMMA}} = 0.037$,[16,22] we obtain predictions of the interfacial width for PBD and PMMA. These predictions are compared with the experimental results in Table 2. Of course we should not necessarily expect the Helfand theory to predict interfacial widths for brushes, because it was derived for the interface between semi-infinite homopolymer layers and does not take account of the perturbation introduced by the wall.

Several points should be noted when comparisons are made between these values. First, the molecular weight appears to have little affect on the interface width. This

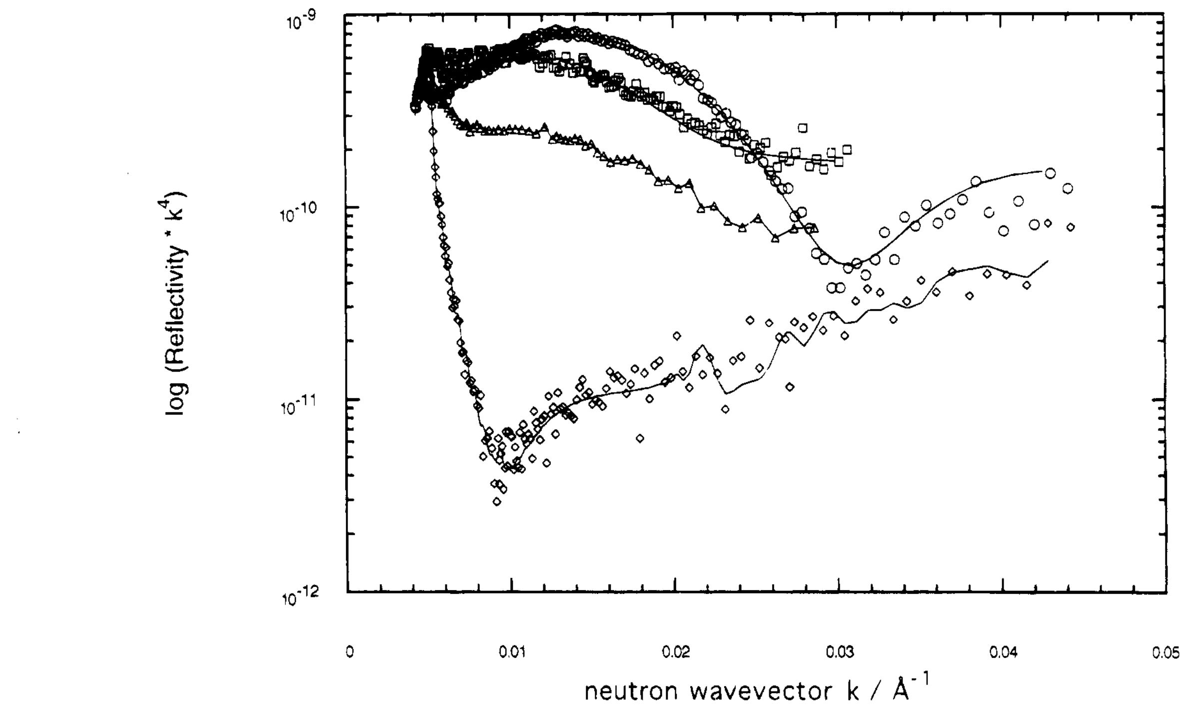

Figure 2. Reflectivity data (symbols) and the best fits (lines), plotted as reflectivity × k^4, for a range of matrix polymers: 10k PBD (circles), 500k hPS (squares), hPS/PPO blend (triangles), and PVME (diamonds).

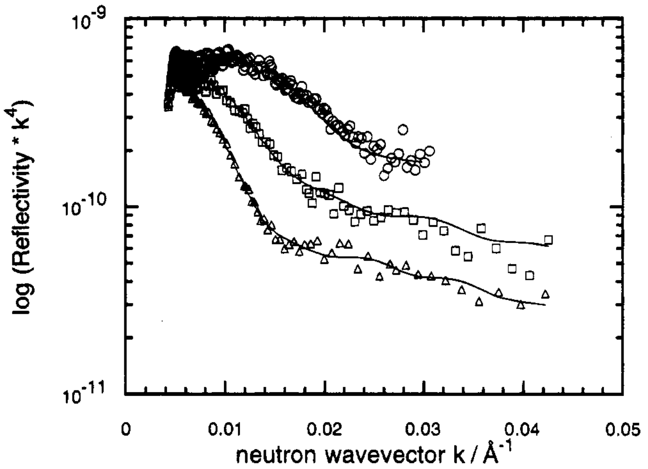

Figure 3. Reflectivity data and best fits (lines) for three different molecular weight polystyrenes: 500k (circles), 29k (squares), and 7k (triangles).

can be seen by comparing the widths for 10k and 540k PBD; the molecular weight has increased by a factor of 50, but the experimental widths are almost identical. Therefore it is valid to make comparisons with the result of Genzer[14] for an intermediate molecular weight. Similarly, different molecular weights were used in the PS–PMMA interface width measurements of Anastasiadis et al.,[16] Fernandez et al.,[15] and Bucknall et al.,[17] but their results are all consistent. It is apparent therefore that molecular weight is not an important parameter in this situation. Second, it is necessary to take account of the change of the interaction parameter with annealing temperature. This also has only a small affect on the predicted interfacial width, typically <3 Å over the range of annealing temperatures used by different experimenters.

There is a clear trend in the table; the brush experiments have a larger width than the homopolymer and block copolymer experiments, which in turn are larger than the theoretical predictions. The Helfand prediction is known to underestimate the experimental widths.[16]

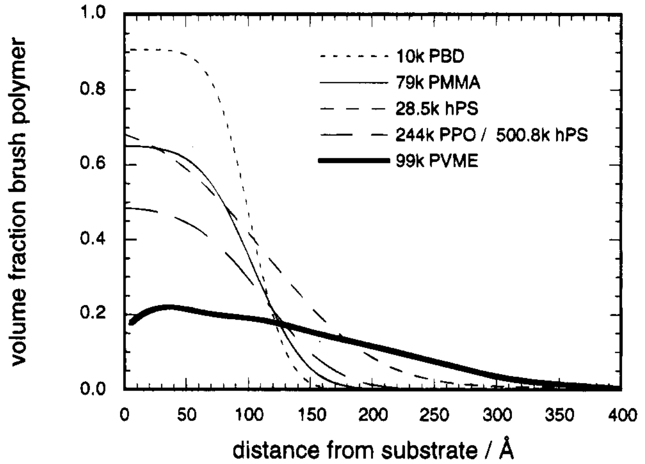

Figure 4. Equilibrium brush profiles for matrix polymers which are immiscible (PBD and PMMA), neutral (hPS), and favorably interacting (PPO/hPS blend and PVME).

Table 2. Comparison of Experimental and Predicted Interface Widths (Å)

	PBD (10k)	PBD (540k)	PMMA
These Experiments			
	53 ± 4	53 ± 4	84 ± 4
Other Experimental Results (Homopolymers and Block Copolymers)			
Genzer et al.[14]	32		
Anastasiadis,[16] Fernandez,[15] Bucknall[17]			50
Theoretical Predictions			
Mean Field (eq 4)	18	17	31
Mean field + fluctuations (brush)	23		36
Mean field + fluctuations (homopolymers)	33		51

Theories that take account of chain end effects and fluctuations in the interface[23,24] predict larger values. These fluctuations represent a spatial variation of the position of the interface and are averaged by neutron

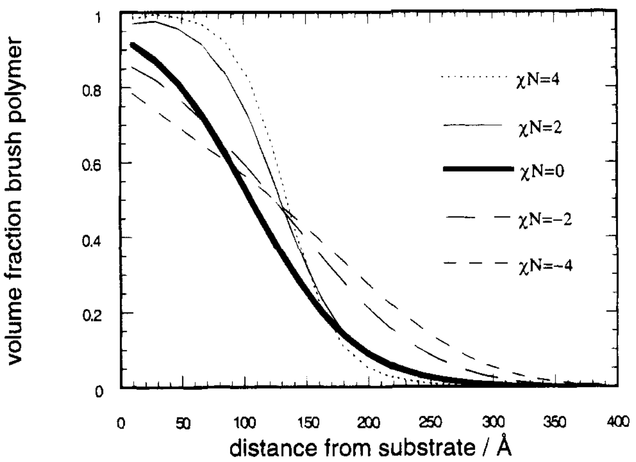

Figure 5. SCF brush profiles (for brush chains of 80 000 molecular weight) with values of χN_{brush} between −4 (miscible) and 4 (immiscible).

reflectivity experiments. Table 2 also shows the effect of including fluctuations in the predicted interface width for brushes. The correction due to fluctuations is much smaller for brushes than for homopolymer interfaces. This is because the fluctuations are suppressed when one of the chain ends is tethered to a flat surface. The table shows that the measured values of the interfacial width for immiscible homopolymers are entirely consistent with the Helfand predictions when the effects of interfacial fluctuations are taken into account.[24] However this is not the case for brushes. Brushes are different from homopolymer interfaces because of the large number of chain ends present in the brush. Therefore we would not necessarily expect the experimental brush widths to be the same as widths from homopolymer experiments.

Figure 5 shows the effect of varying χN_{brush} on the SCF brush profiles for a range of values between 4 (immiscible) and −4 (miscible). Here N_{brush} corresponds to a brush molecular weight of 80 000, which matches the experimental value, and $N_{\text{matrix}}/N_{\text{brush}} = 4$. As χN_{brush} increases, the interfacial width of the SCF profiles decreases. It was not possible to produce SCF profiles to match the experiments because the program does not produce a stable solution for large values of χN_{brush} $(>\sim 10)$. However an SCF profile with $\chi N_{\text{brush}} = 5$ already has a narrower width than the experimental profile for the 10k PBD matrix (which has $\chi N_{\text{brush}} = 80$), and in the limit of large χN_{brush} we expect the SCF theory to regain the Helfand result.

It is clear from Figure 5 and from Table 2 that the experimental brush interface widths are larger than the numerical SCF and Helfand predictions, even when fluctuations are taken into account. This suggests that there must be some other effect which causes the large experimental widths. One possible explanation of this is the presence of lateral inhomogeneities in the brush. Yeung, Balazs, and Jasnow[25] have predicted that a homogeneous grafted layer in a poor solvent is unstable and can form a dimpled surface. Dimpling would lead to an increased apparent width from reflectivity experiments in the same way as fluctuations do. Furthermore, dimpling can cause off-specular neutron scattering that could be observed with an appropriate experimental setup. No significant off-specular scattering was observed from the brush/PMMA or brush/PBD samples in this experiment. However we have observed large off-specular scattering from brushes of physically end-adsorbed dPS in a low molecular weight PMMA matrix.

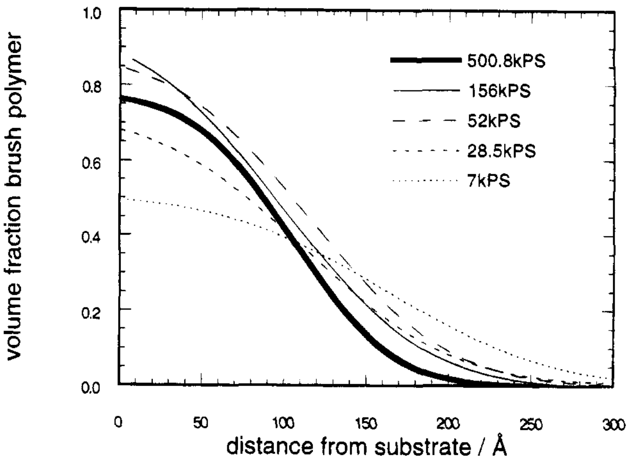

Figure 6. Brush profiles for a range of different molecular weight polystyrene matrices.

We conclude that the nature of the interface between a brush and an immiscible matrix is different from those of the interface between two homopolymers. This could be due to dimpling of the brush. Substantially greater mixing appears to take place when the brush is present. This may have important commercial implications for composite materials and polymer compatibilizers, since the extra mixing could enhance material properties such as adhesion.

Neutral Matrix. The brush profiles for polystyrene matrices of molecular weight 7k, 28.5k, 52k, 156k, and 500.8k are shown in Figure 6. The brush profile, in particular its height, is given by a balance between stretching energies and excluded volume interactions between the chains in the brush. A scaling analysis due to de Gennes[26] and developed by Leibler[27] for block copolymers predicts two limiting cases corresponding to very low and very high matrix molecular weights. These regimes can also be studied with numerical SCF theory. For low molecular weights ($N_{\text{matrix}} < N_{\text{brush}}^{1/2}$) there is a large entropic penalty associated with excluding matrix molecules from the brush. Their concentration in the brush is therefore quite high and the brush is wet. As the molecular weight of the matrix increases, the amount of matrix polymer in the brush decreases until, when $N_{\text{matrix}} \sim N_{\text{brush}}$, a limiting dry brush form is reached for which a further increase in the matrix molecular weight does not affect the properties of the brush. A dry brush however still contains an appreciable amount of solvent polymer.

These predictions have previously been investigated by Zhao et al.[2] and Budkowski and co-workers[29] for physically adsorbed brushes. They both used experimental techniques (secondary ion mass spectrometry and ^{3}He nuclear reaction analysis respectively) whose resolution is not sufficient to determine the detailed features of the brush profile. However they were both able to measure a brush thickness parameter as a function of the molecular weight of the matrix and grafting density. Zhao et al. observed no significant difference in their brush thickness for matrix molecular weights of 500k and 7k (with brush molecular weights of 13k−43k), and they claim that if $N_{\text{matrix}} > N_{\text{brush}}^{1/2}$, the concentration profile is independent of molecular weight. However, in their experiments, the samples with different matrix molecular weights were annealed at very different temperatures (108−106 °C) and had

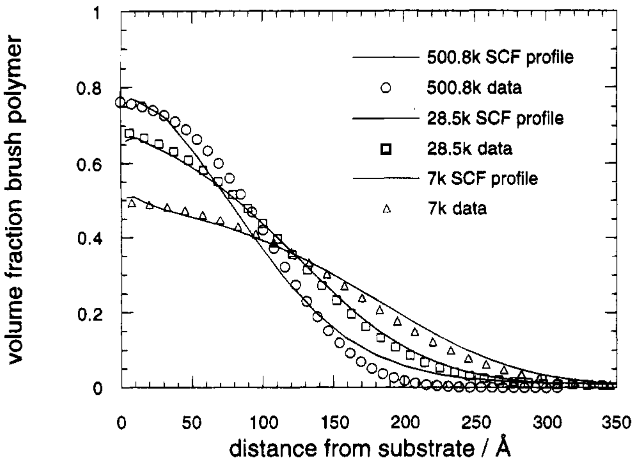

Figure 7. Comparison of experimental profiles (symbols) and numerical mean field profiles (solid lines) for a set of different molecular weight polystyrene matrices: 7k, 28.5k, and 500.8k.

very different surface coverages. Budkowski et al. have shown that the surface coverage has an effect on the measured brush thickness. They state that for $N_{\text{matrix}} > N_{\text{brush}}^{1/2}$, excluded volume interactions are screened out and the stretching of the brush chains will be modulated by N_{matrix}. They have observed a decreasing brush thickness as the matrix molecular weight is increased from 9.2k to 330k (at approximately constant grafting density).

The discrepancy between previous work demonstrates that more precise measurements of, and theoretical predictions for, the whole brush profile are needed. We have kept the grafting density constant by using chemical grafting which simplifies the situation considerably. Neutron reflectivity enables us to determine the whole brush profile, and not just a measure of the height. Third, we have made detailed comparisons with profiles derived from numerical SCF theory. Scaling theory is not best suited to this situation because in many of the experiments we are not really in either the wet or dry brush regimes but in a crossover region. The combination of these three makes it possible to produce more precise results and comparisons with theory.

The highest molecular weight used (500.8k) was chosen to be in the dry brush regime. The strong effect of the matrix molecular weight for $N_{\text{matrix}} < N_{\text{brush}}$ contrasts with the immiscible polymer matrix, for which the matrix molecular weight had very little effect on the profile. Figure 6 shows that the differences between the profiles for the 52, 156k, and 500.8k hPS matrices are relatively small and are partly due to small differences in the total amount of grafted polymer. Therefore we have observed the onset of the dry brush regime when $N_{\text{matrix}} \sim N_{\text{brush}}$, as expected.

The experimental profiles are shown in Figure 7 for three molecular weights together with profiles derived from numerical solutions of the SCF equations.[7] The numerical solutions have only one adjustable parameter, the sticking energy. In this case the actual value of the sticking energy has no physical significance since it is only used to match the experimental grafting density, which is fixed by the grafting process and not by an equilibrium with functionalized polymer in the bulk. There is extremely good agreement between the experimental and calculated profiles, although the mean field profiles are slightly broader than the experimental ones in each case. Since this slight discrepancy was also observed by Jones et al.,[9] we suggest that though the numerical solutions of the SCF equations are extremely good, the mean field theory cannot completely account for the experimental results. This may be due to a breakdown in the basic mean field approximation; i.e. the replacement of the actual chain statistics by appropriate averages. The effect of this averaging is known to be negligible for homogeneous blend systems, where the chain statistics found from scattering experiments are in good agreement with the mean field predictions of Gaussian chains[28] (i.e. the random phase approximation). However, the perturbation in these statistics in the presence of strong spatial inhomogeneities introduced by the wall may invalidate the mean field assumption.

The effect of in-plane brush height fluctuations is less apparent for a neutral matrix than for the immiscible matrix. Fredrickson et al.[30] have calculated the modes which will contribute to the fluctuations by assuming that all the ends of the brush chains lie at the interface. They derive the same result as Semenov[23] and Shull, Mayes, and Russell[24] for the immiscible case and speculate that large amplitude fluctuations would be observed if the interfacial tension is reduced because the polymers are less immiscible. However calculations in this regime indicate that the root mean square amplitude of the fluctuations is ~2 Å.[31] Therefore they will produce only a very small increase in the experimental interfacial width. Since the experimental and SCF profiles are in extremely good agreement for a range of interfacial widths (~100–300 Å), it seems likely that the effect of the fluctuations is indeed small. Of course, they will become insignificant for favorably interacting matrix polymers, where it becomes hard to define the position of the interface precisely.

In summary, our experiments are in good agreement with the predictions of numerical SCF theory, and also reflect the wet and dry brush regimes predicted by scaling theory. Neutron reflectivity experiments have shown that (at constant grafting density) the width of the interface between the brush and the matrix depends on the molecular weight of the matrix. The height of the brush (defined by the offset of the error function profile) does not change with the matrix molecular weight of the matrix. Swelling of the brush by low molecular weight matrix chains leads to a broader profile (i.e. a larger interfacial width between the brush and the matrix), and the brush chains extend into the matrix. Previous experiments did not have sufficient resolution to observe this in detail.

Favorably Interacting Matrix Polymers. In a favorably interacting matrix, brush chains are expected to stretch out into the bulk and the volume fraction of the matrix polymer in the brush is expected to be much higher than in an immiscible matrix. This is confirmed by the profiles shown in Figure 4. The PPO/hPS blend profile shows the expected trend. The large polydispersity of the PPO ($M_w/M_n \approx 7$) makes it impossible to produce representative numerical SCF profiles. Therefore no detailed comparisons can be made with the experimental profile.

In the PVME matrix, the brush chains extend several hundred angstroms into the bulk and are highly stretched (the unperturbed radius of gyration of the grafting polymer is 73 Å). A numerical SCF profile is compared with the experimental one in Figure 8. The SCF theory uses a value of χ which is not concentration dependent. However χ is known to increase (i.e. become less negative) as the volume fraction of dPS in-

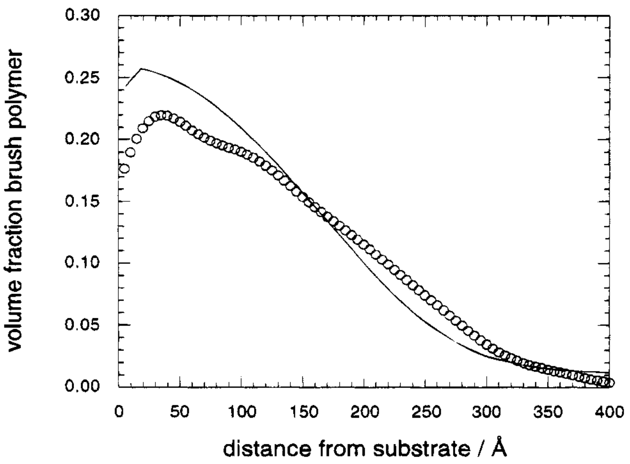

Figure 8. Comaparison of the experimental profile (circles) and numerical mean field profile (solid line) for 99k PVME.

creases.[32-34] Therefore the brush and matrix are more miscible at low volume fractions of brush polymer. The concentration dependent interaction parameter could therefore account for the tail on the experimental profile, which is significantly extended in comparison to the SCF profile. Also, the PVME is polydispersed ($M_w/M_n \approx 2$) whereas the SCF equations assume monodispersity.

Since the brush profile in PVME is not an error function, but a free form maximum entropy profile, it is not easy to define the height or interfacial width of the brush. We have estimated it as the distance between the points at which the volume fraction of dPS has 10% and 90% of its maximum value. This is roughly equivalent to the standard definition when the profile is a hyperbolic tangent and gives an interfacial width of about 300 Å. Similarly, the height of the brush (simply defined in this case as the distance from the substrate at which the volume fraction of brush polymer has dropped to half of its maximum value) is approximately 200 Å. There is a maximum in the NR profile about 30 Å from the substrate, which was also observed by Jones et al.[9] The reason for the maximum could be the slight preference of the PVME segments for the silicon oxide layer on the substrate. This can be included in the SCF theory by adding a favorable matrix monomer−substrate interaction energy of about $0.05k_BT$. A maximum can be included in the error function profile (eq 1) but was not found to improve the fits for any of the other matrix polymers.

Brown, Char, and Deline[35] have predicted for miscible polymers that the brush height, h, scales as

$$h \sim \left(\frac{-\chi}{2}\right)^{1/3} N a \sigma^{1/3} \tag{5}$$

where χ is the interaction parameter, N the degree of polymerization of the brush polymer, a its step length, and σ the grafting density (in units of a^{-2}). The grafting density was determined from ellipsometric measurements of the grafted layer thickness before the matrix is added. Using the above expression, with an estimate of χ for the dPS/hPS−PPO system as a mean of $\chi_{\text{hPS-dPS}}$[36] and $\chi_{\text{PPO-dPS}}$,[37-40] we obtain a height of about 200 Å for both PVME and PPO/hPS. This compares with experimental values of ~200 and 112 Å, respectively. It is not surprising that the brush height is greater in the PVME matrix than in the PPO/hPS blend because PVME is more miscible with PS than PPO, and there is also a small difference in the grafting density. The predictions of the scaling law are therefore of the same order of magnitude as the experimental values. We should not expect precise agreement anyway as the scaling arguments only predict trends and cannot provide the prefactor for eq 5.

Conclusions

A method for chemically grafting polymers only a silicon substrate has been developed. The segment density profiles of the grafted chains have been determined as a function of depth normal to the sample by neutron reflectivity. In this way we have investigated the effect of matrix polymer miscibility and molecular weight on the conformation of the brush chains.

We find that the width of the interface between the brush and matrix is narrow for immiscible polymers and increases as miscbility increases. For favorably interacting polymers, the brush chains stretch out to several times their radius of gyration. For the neutral matrix, the brush profile depends strongly on the matrix molecular weight when the matrix molecular weight is less than that of the brush and is independent of it at higher values. We have observed the transition between the wet and dry brush regimes predicted by Leibler and Shull.

The experimental interfacial width has been compared with the theory of Helfand and Tagami[18] (with corrections for different segment lengths[19] and finite molecular weight[20]). The experimental widths were significantly larger than predicted, even when capillary wave fluctuations in the position of the interface are taken into account, and also larger than widths from homopolymer and block copolymer experiments. This may be at least in part due to lateral dimpling or clumping in the brush. We conclude that the interface between a brush and a homopolymer is substantially different from homopolymer−homopolymer interfaces. In particular, there appears to be more mixing when a brush is present, which may have important commercial implications.

Comparisons have also been made with numerical self-consistent field simulations for neutral and favorably interacting polymers, and very good agreement has been found. For favorably interacting polymers, we found reasonable agreement with numerical SCF theory and order of magnitude agreement with a scaling law for the height of the brush.

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(13) The standard (Helfand) definition of the interface width, a_I, is twice the width (w) of a hyperbolic tangent profile, tanh(x/w). tanh(x/w) and erf(x/s) are almost identical if $s = (2/\sqrt{\pi})w$ (the gradients are equal at $x = 0$). Therefore we can write $a_I = 2w = s\sqrt{\pi} = 1.77s$.

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