Configuration of Grafted Polystyrene Chains in the Melt: Temperature and Concentration Dependence

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The concentration profiles of carboxy-terminated polystyrene chains in the melt grafted onto oxide-covered silicon substrates were measured using secondary-ion mass spectroscopy. The grafting density increased with temperature and an enthalpy of $+7.4$ kcal/mole was deduced for the grafting reaction, $SiOH + R(COOH) \rightleftarrows R(COOSi) + H_2O$. Relatively high grafting densities ($\sigma \sim 6.6 \cdot$ mg/m^2) were achieved with minimal chain distortion or displacement of long chains by shorter ones. Significant stretching of the grafted chains occurred for $\sigma > 10$ mg/m^2. An equilibrium constant for the grafting reaction incorporating entropy is discussed.

Because of their many practical applications, grafted polymer chains have been the subject of intensive theoretical [1-3] and experimental [4-8] research. An important consideration in all these studies has been the enthalpy of attachment since, in order to produce a stable grafted configuration, the enthalpy of attachment must be greater than the energy of mixing between the polymer chains and the solvent matrix. The different theoretical models, reviewed by Milner [9], for the grafting dynamics of adsorbed polymers are mainly applicable to stretched chains in dilute solutions. This limit is not appropriate for anchored chains in a melt where, due to screening of the excluded-volume interaction and the constraint of constant polymer density, the stretching of the chains is greatly reduced. Numerical calculations for melts, based on self-consistent lattice models, have recently appeared and are reported to work well in the dense brush regime such as that obtained with block copolymers at interfaces [3,10]. In order to test these and other models, it is essential to identify the mechanism of the chain attachment, and measure the resulting chain conformations and kinetics. This is achieved most conveniently using the technique of secondary-ion mass spectrometry (SIMS), which directly measures the concentration as a function of depth in a model-independent manner for various molecular species with a depth resolution of approximately 100 Å [11,12].

In this paper we discuss the system of carboxy-terminated polystyrene or deutero-polystyrene chains, PS(COOH) and dPS(COOH), respectively, grafted onto Si-oxide-covered substrates in blends with either deuterated polystrene (dPS) or polystyrene (PS). This system was chosen since polymers capped with carboxylic acid were shown to be far less prone to associate into clusters than those with zwitterion or amine ends [13]. Furthermore, for the molecular weights used in this study the chemical interactions between the grafted and matrix

chains are minimal [14], simulating as closely as possible ideal conditions in a melt. On the other hand, by being able to profile complementary combinations of end-grafted dPS in a PS matrix or end-grafted PS in a dPS matrix, we were able to observe the effect of the preferential interactions between the oxide-covered [15,16,17] substrate and the monomers in the grafted chains or those of the matrix. The temperature dependence of the grafting density was studied using blends consisting of 10%, by volume, hydrogenated polystyrene (PS) ($M_w/M_n < 1.1$) of molecular weights 13000, 22000, and 48000, functionalized with a COOH unit, and 90% monodisperse deuterated polystyrene chains of molecular weight of either 7000 or 500000. Films approximately 2000 Å thick were spun cast from toluene solutions directly onto oxide-covered silicon substrates and annealed in a vacuum of 10^{-5} Torr for 36 h above the glass transition ($T_g = 100$ °C) at 108, 135, 160, and 235 °C. The dependence of the grafting density on bulk concentration was measured either by spin coating dPS(COOH) ($M_w = 104000$, $M_w/M_n < 1.1$) and PS ($M_w = 670000$, $M_w/M_n < 1.1$) blends from toluene solution directly onto oxide-covered Si substrates or by floating a layer of PS on top of another layer of dPS(COOH) previously spun directly onto the Si substrate. In both cases the total initial volume fraction, ϕ_{init}, of dPS(COOH) ranged from 0.01 to 0.33. The samples were annealed in a vacuum of 10^{-5} Torr at 160 °C for at least 48 h to ensure that the profiles were at equilibrium. This was confirmed by the fact that the SIMS profiles of samples with the same total ϕ_{init} were similar in grafting density and distribution regardless of the method of preparation. The details of the SIMS analysis are described in Ref. [12].

Figure 1 is a plot of the concentration profiles $\phi(z)$ obtained by detecting the CH$^-$ ion yield as a function of distance from the Si-oxide substrate for a $M_w = 48000$ PS(COOH) blend annealed at various temperatures.
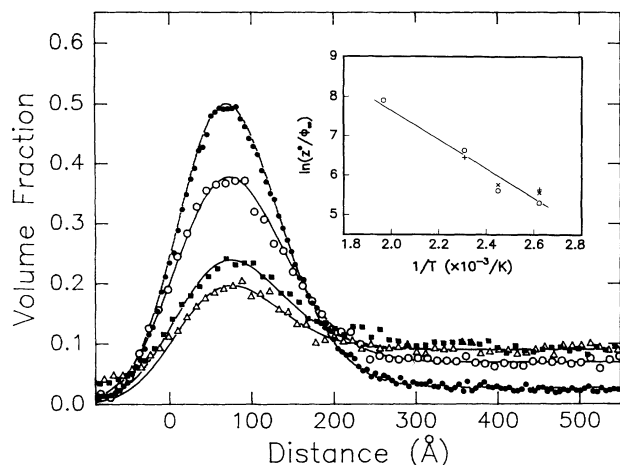
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FIG. 1. Volume fraction of PS(COOH) (M_w =48 000) derived from the CH$^-$ intensity in a dPS matrix annealed for 48 h at T =235°C (●), 160°C (o), 135°C (■), and 108°C (△). Inset: $\ln(Z^*/\phi_\infty)$ vs inverse temperature for PS(COOH) of M_w =48 000 (o), M_w =22 000 (×), and M_w =13 000 (+) in a dPS matrix.

The position of the interface (z =0) to which the COOH end is grafted was determined by the position of the SIMS oxygen peak on the silicon surface. The solid lines are fits (convolved with a Gaussian resolution function [12] of FWHM = 100 Å) by an analytical approximation for a chain with one segment attached to a wall and the remaining segments undergoing a random walk on a lattice [18–21], as discussed in more detail in Ref. [7].

From Fig. 1 one can see that Z^*, the total integrated surface excess, increases markedly with temperature as would be expected if the ends were reacting chemically with the silica surface. If adsorption of the end functionalized group was the predominant mechanism for attachment, then the rate of desorption would increase with temperature and Z^* would be reduced. A probable grafting mechanism for the chain ends to the surface is via an esterification reaction of the functional end with SiOH groups present in the silicon-oxide layer [22,23]:

$$R(\text{COOH}) + \text{SiOH} \rightleftharpoons R(\text{COOHSi}) + H_2O , \qquad (1)$$

where R represents the polymer chain. Here the carboxyl end group and the silanol are respectively the acid and alcohol groups which react to liberate water and form the R(COOSi) ester. The need for an oxide layer to provide the points of attachment was confirmed by experiments which showed almost no functionalized chains on silicon substrates where the oxide layer was removed by HF acid etching [17]. The reduced value of Z^* measured on the RTA substrates is consistent with the reduced number of SiOH units present on silica surfaces which were prepared by heating above 600°C, where significant desorption of OH groups occurs [16]. The equilibrium constant K for this reaction [23] can be expressed in terms of the concentration ratios by

$$K = \frac{[H_2O]}{[\text{SiOH}]} \frac{[R(\text{COOSi})]}{[R(\text{COOH})]} = C_0 e^{-(\Delta H - T\Delta S)/kT} , \qquad (2)$$

where C_0 is an arbitrary constant, ΔH is the enthalpy change of the reaction, and ΔS is the change in entropy between a reacted and an unreacted chain. The concentration of the ester, $[R(\text{COOSi})]$, is simply the grafted chain density, which is proportional to Z^*, and the concentration of unreacted R(COOH) is proportional to the volume fraction of unattached chains in the bulk, ϕ_∞. If we assume that the density of OH groups on the silicon-oxide surface is similar to that previously measured on silica and glass particles [16], approximately three to five groups per 10^2 Å^{-2}, then the concentration on the surface is to first order unaffected by the attachment of the polymer chains whose grafting density, $\sigma = Z^*\rho/N$ (where ρ is the density of polystyrene and N is the polymerization index of the grafted chain), is on the order of 10^{-3} Å^{-2}. Similarly, the H_2O concentration is unaffected since it is primarily determined by the base pressure of the vacuum system. The equilibrium constant K becomes proportional to the ratio of the experimentally measured quantities Z^* and ϕ_∞ and Eq. (2) can be rewritten as

$$\ln(Z^*/\phi_\infty) = -\Delta H/kT + \ln(C_0) + \Delta S/k . \qquad (3)$$

The inset to Fig. 1 is a plot of $\ln(Z^*/\phi_\infty)$ as a function of inverse temperature. The best fit to the data yields a straight line with a slope of -3709 K, corresponding to ΔH of $+7.4$ kcal/mole. The sign of the slope indicates that this reaction is endothermic and is driven towards formation of the ester by pumping away the H_2O [22].

As can be seen from Fig. 1, the thickness of the grafted layer was roughly $2R_g$, or approximately equal to the diameter of a dPS molecule, for all the temperatures studied. Therefore ΔS associated with the grafting reaction for the range of σ studied is small compared to ΔH. This is also indicated in the inset of Fig. 1 where the data for $\ln(Z^*/\phi_\infty)$ vs $1/T$ are a straight line whose slope is independent of molecular weight. Consequently, since the grafting reaction does not change the chain conformation, no preferential displacement of longer chains by shorter ones should occur in this limit.

To test this hypothesis, we first grafted a thin (300 Å) layer of M_w =104 000 dPS(COOH) "long" chains onto a native-oxide-covered silicon substrate by annealing at 160°C. This layer was then covered with a 3000-Å-thick layer consisting of a blend of 0.90 PS (M_w =670 000) and 0.10 PS(COOH) "short" chains (M_w =12 000) and annealed further at 160°C for approximately 50 h. The bilayer concentration profile is shown in Fig. 2, together with the profile for a ϕ_{init} =0.10 dPS(COOH)/PS blend also annealed for 50 h, to which no short-chain end-labeled polymers were added. The Z^* values for the bilayer and blend samples were 90 ± 5 Å and 107 ± 5 Å, respectively. Consequently the fraction of long chains displaced is no larger than 20%. These results are in con-
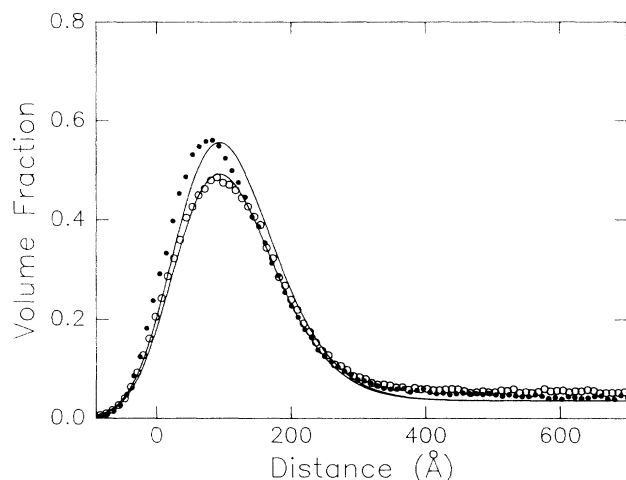
FIG. 2. Volume fraction of dPS(COOH) ($M_w = 104000$) derived from the D^- intensity for (O) a blend of dPS-(COOH)/PS ($M_w = 670000$) having $\phi_{init} = 0.10$ and (●) a bilayer corresponding to $\phi_{init} = 0.10$ (see text), but where the matrix consists of 0.10 PS(COOH) ($M_w = 12000$) and 0.90 PS ($M_w = 670000$). The solid lines are fits by Eq. (1) with $R_g = 84$ Å. Both samples were annealed for 50 h at 160 °C.

trast to similar experiments performed on grafted chains in solution where complete substitution of the longer chains was reported [24]. As a result of the excluded-volume interaction, the chains in solution are distorted [5], even at low grafting densities. Since $\Delta S < 0$ in this case, the entropic penalty is minimized when short chains are preferentially grafted at the interface. In our case, ΔS is negligible, and although the profile for the shorter PS(COOH) chains cannot be determined in these experiments separately from the PS matrix, it is reasonable to assume that in order to satisfy Eq. (3) for Z^*/ϕ_∞, they simply graft beside the longer dPS(COOH) chains. This can be seen in Fig. 2 where the profile of the dPS-(COOH) chains in the bilayer sample is slightly shifted from the Si-oxide interface [25].

In order to induce the chains in the melt to stretch, much higher grafting densities must be achieved than

TABLE I. Summary of data for dPS(COOH)/PS [a] blends.

ϕ_{init}	ϕ_∞	Z^* (Å)	W (Å)	σ (10^{-3} Å^{-2})	σ (πR_g^2)
0.0083	0.0034	16	71 ± 10	0.093	2.05
0.05	0.017	66	71 ± 4	0.38	8.5
0.094	0.035	107	110 ± 5	0.62	14
0.154	0.066	179	126 ± 5	1.04	23
0.19	0.093	214	145 ± 5	1.24	27
0.22	0.10	229	142 ± 6	1.33	29
0.29	0.166	303	181 ± 7	1.75	39
0.34	0.185	277	268 ± 6	1.61	35
0.196 [b]	0.136	179	182 ± 5	1.04	23

[a] PS of $M_w = 670000$ unless otherwise stated.
[b] Matrix consists of 0.40 PS of $M_w = 670000$ and 0.40 PS of $M_w = 1700$.

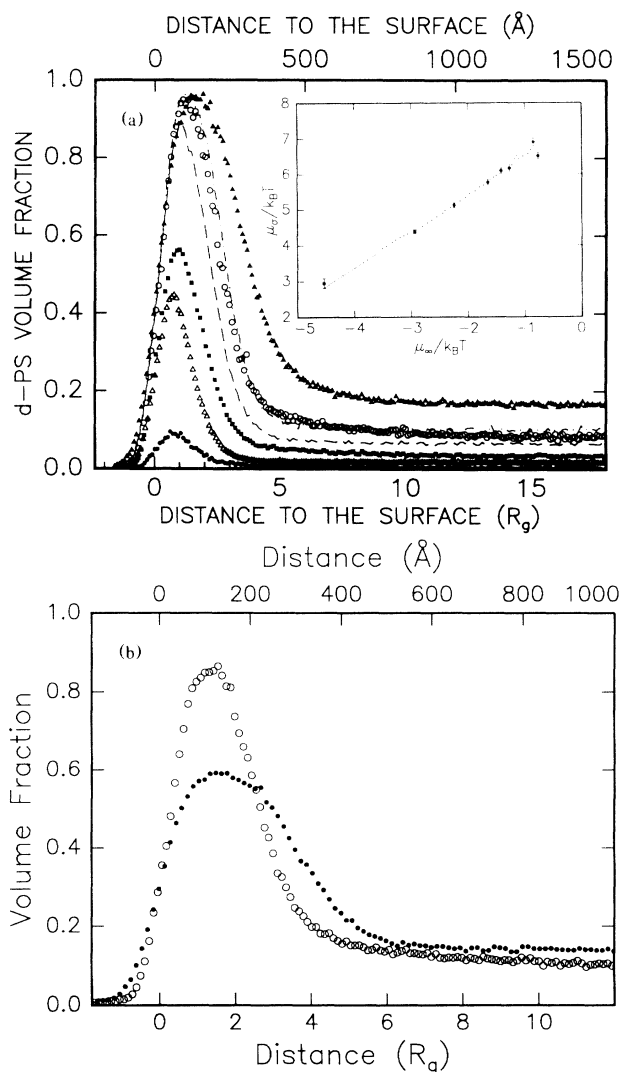FIG. 3. Volume fraction of dPS(COOH) derived from the D^- ion intensity from blends of dPS(COOH) and PS ($M_w = 670000$) annealed at $T = 160$ °C for 50 h or longer. (a) Concentration profiles from blends having initial volume fractions ϕ_{init} of dPS(COOH) of 0.083 (●), 0.05 (△), 0.094 (■), 0.19 (O), and 0.29 (▲). The dashed lines correspond to bilayer samples of $\phi_{init} = 0.154$ and 0.22. (b) Concentration profiles of $\phi_{init} = 0.20$ blends of dPS(COOH) with 0.80 PS ($M_w = 670000$) (O) and 0.40 PS ($M_w = 670000$) plus 0.40 PS ($M_w = 1700$) (●). Inset to (a): μ_σ vs μ_∞ (see text) for the profiles shown in (a) (●) and in (b) (△).

those previously obtained [5] in solution. From Eq. (3), we see that this can be done by increasing ϕ_∞. The results for samples prepared from either blends or bilayers annealed at $T = 160$ °C for times longer than 58 h are shown in Fig. 3(a). The quantities σ, ϕ_∞, and W, the half-width of the layer, are tabulated in Table I. Assuming a monomer density [26] of $\rho = 5.4 \times 10^{-3}$ Å^{-3}, one can approach a packing density for a polystyrene melt of $M_w = 104000$ of approximately 22 chains in a cylinder of radius R_g and length $2R_g$ (the thickness of the un-

stretched layer). Consequently, one can see from both Fig. 3(a) and Table I that when the number of chains grafted in an area πR_g^2 approaches this estimate, the chains are forced to stretch as a result of the melt incompressibility.

The effect of stretching on the grafting density should be governed by Eq. (2). An equivalent formulation is to start from the Gibbs free energy and equate the chemical potentials, μ_σ and μ_∞, of the grafted and ungrafted chains, respectively. The chemical potential of the attached chains can be approximated [27] by

$$\frac{\mu_\sigma}{kT} = \ln(\sigma a^2) + \frac{3}{2}\frac{r^2}{a^2 N} + \frac{\Delta H}{kT}, \tag{4}$$

where $a = 6.7$ Å, or the PS Kuhn length [14], and the first two terms are derived from the occupational and stretching entropy of the individual chains. Since we do not have an exact solution for the conformation profile, we take the mean position of the nongrafted end, r, to be approximately equal to W. The chemical potential of the unattached chains is similar to that used by Shull [3],

$$\frac{\mu_\infty}{kT} = \ln(\phi_\infty) + (1 - \phi_\infty)(1 - N/N') + (1 - \phi_\infty)^2 N\chi, \tag{5}$$

where $\chi = (1.7 \pm 0.4) \times 10^{-4}$ is the Flory interaction parameter [14] and N' is the degree of polymerization of the matrix. The inset in Fig. 3(a) is a plot of μ_σ vs μ_∞ calculated from the data in Table I, where the fitted slope is 1.03 ± 0.05.

In order to further test the validity of this formulation, we prepared a bilayer sample corresponding to $\phi_{init} = 0.20$, but where the matrix layer was composed of 0.40 PS of $M_w = 670000$ and 0.40 PS of $M_w = 1700$. From Fig. 3(b), we see that, as expected by mean-field theory [21], the shorter chains swell the grafted layer. The resulting entropy loss comes at the expense of removing some of the grafted chains from the substrate into the bulk. Substituting the measured values of σ and ϕ_∞ into Eqs. (4) and (5) we see from the inset that the experimental point (triangle) agrees well with the predicted value.

In conclusion, we have determined that carboxy-terminated polystyrene chains grafted in the melt differ from those grafted in solution near room temperature in several respects [5,9,24]. The chains react with the substrate via an endothermic reaction, rather than being adsorbed. Relatively high grafting densities ($\rho Z^* = 6.6$ mg/m^2) could be obtained without significant stretching of the chains. Only minimal displacement of long grafted chains by shorter ones occurs. In order to maintain constant density the grafted layer is observed to stretch when $\rho Z^* > 10$ mg/m^2.

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[25] It should be noted that when the grafted chains are deuterated, the dPS monomers are preferentially attracted to the oxide-covered substrate. This results in a slight distortion of the profile not observed with the PS(COOH) chains. This is shown in Fig. 2 where the solid line corresponds to a fit by the expression discussed in Ref. [7] for a tethered Gaussian chain and the usual $R_g = 84$ Å. A good fit is obtained only for the bilayer sample, where the short PS(COOH) chains graft onto the substrate and essentially screen out the interaction.

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[27] To derive Eq. (4) from the Gibbs free energy (see Ref. [23]) one should also include the chemical potentials corresponding to the H_2O and OH concentrations. As discussed in the text these quantities are independent of the polymer concentration and therefore do not affect the slope in the inset of Fig. 3(a), but merely shift the intercept. In addition, the term corresponding to the interchain enthalpic interaction is small within the brush and was omitted.