Polystyrene Layers Grafted to Macromolecular Anchoring Layer

K. Swaminatha Iyer,† Bogdan Zdyrko,† Hauke Malz,‡ Jürgen Pionteck,‡ and Igor Luzinov*,†

School of Materials Science and Engineering, Clemson University, Clemson, South Carolina 29634, and Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

Received April 10, 2003; Revised Manuscript Received June 12, 2003

ABSTRACT: Dense and homogeneous grafted polymer layers were anchored from the melt onto a silicon wafer modified with a macromolecular anchoring layer rich in epoxy functional groups. A monolayer of poly(glycidyl methacrylate) (PGMA), attached to silicon wafers, served as the macromolecular anchoring layer. Carboxylic acid- and anhydride-terminated polystyrenes (PS) of different molecular weights were used for the grafting. The grafted layers did not dewet at elevated temperatures and did not desorb in a good solvent under ultrasonic treatment. Comparison of the results for the grafting to the PGMA primary layer with literature data obtained for the grafting to the epoxysilane monolayer suggested that there were many similarities between these grafting processes. The same major trends were observed. However, the grafting to the PGMA layer was much more effective. We attribute the high efficiency of the PGMA anchoring layer in the grafting reactions to the high mobility of the epoxy reactive groups and formation of an interpenetrating zone at the PS/PGMA interface.

Introduction

Synthesis of end-grafted polymer layers on a solid substrate is an effective way to control surface properties such as adhesion,[1] lubrication,[2] wettability,[3,4] friction,[5] biocompatibility,[6] and colloidal stabilization,[7,8] which are very important for various technologies. Factors affecting the preparation and performance of these layers have been the subject of much theoretical[9,10] and experimental research.[11−15] Generally, the behavior of the ultrathin grafted films is strongly dependent on the density of the chain attachment. Dense grafting of the macromolecular chains results in formation of a polymer brush when the chain spacing is under two radii of gyration (R_g) of the grafted macromolecules. When the brush regime is attained, the grafted chains begin to stretch away from the surface to avoid crowding. Because of the confinement and the uniform polymer constitution, the brush reacts collectively to environmental stimuli such as changes of the pH or ion strength, temperature, solvent quality, or mechanical forces.[16] These brush properties provide the basis for fabrication of functional devices on a nanometer scale.

There are several major techniques available for preparation of the grafted layers including physical adsorption of block copolymers,[17] attachment of end-fuctionalized polymers ("grafting to" method),[1,8,12,18] and polymerization initiated from solid surfaces ("grafting from" method).[3,19−21] Each method has advantages and limitations and is more suitable for some applications while less suitable for others. For instance, block copolymer adsorption is a simple and reproducible technique. Nevertheless, it has an important drawback (beside low grafting density), since the immobilized polymers do not remain permanently on the surface. When exceptionally high grafting density is needed, the "grafting from" approach is the only method for brush formation. The polymer brushes grown from the surface by the conventional radical techniques, indeed, possess extremely high density of the attached chains.[20] However, the molecular characteristics of such brushes are not uniform because of their high polydispersity index and chain transfer reactions.[22] Living grafting techniques (anionic and controlled radical) allow synthesis of the well-defined brushes, but the procedure for grafting is more complex and the grafting density obtained by the conventional radical process is not readily achievable.[16,23] In the "grafting to" approach, end-functionalized polymers react with a suitable substrate surface under appropriate conditions to form a tethered polymer brush. The advantage of the method is that well-defined end-functionalized polymers with a narrow molecular weight distribution can be used for the grafting and, as a result, well-defined brushes can be readily synthesized. On the other hand, the technique has a constraint in terms of the maximum grafting that can be obtained, namely that the grafting is self-limiting.[16] The grafting polymer chains must diffuse through the existing polymer film to reach the reactive sites on the surface. This barrier becomes more pronounced as the tethered polymer thickness increases. Thus, the typical polymer brush obtained in this way has relatively low grafting density.

The density of the brush obtained by the "grafting to" method can be increased if the macromolecules attachment is conducted from a melted state.[1,12,24] In fact, the process of polymer grafting to the interface consists of two main regimes.[25] During the first stage the construction of the brush is limited by classical diffusion of polymer chains to the interface. This process is relatively fast, leading to formation of a polymer layer in which chains start to overlap, creating a barrier to further adsorption. The second, slower, regime is characterized by a potential barrier that the macromolecules being grafted have to overcome in order to reach the surface and become anchored. If the grafting is carried out from a melt, many polymer chains are already in location from which they do not need to overpass the potential barrier, since they are already adjacent to the surface. The macromolecules only need to reorient

† Clemson University.
‡ Institute of Polymer Research Dresden.
* To whom correspondence should be addressed: e-mail luzinov@clemson.edu.

10.1021/ma034460z CCC: $25.00
Published on Web 07/23/2003

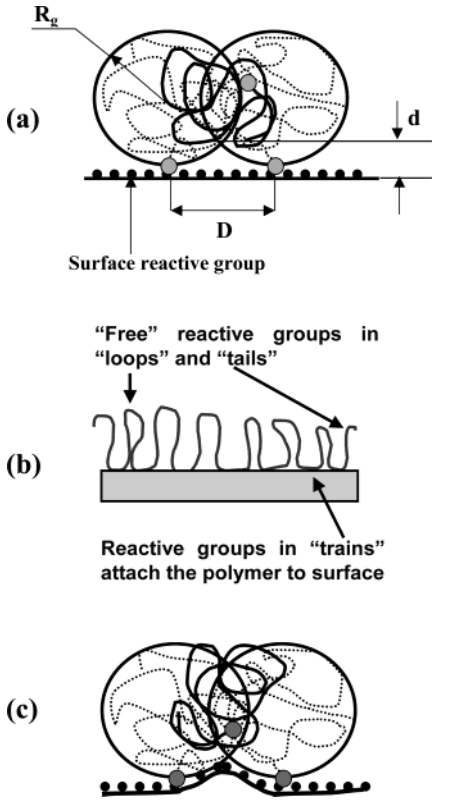

Figure 1. Schematic representation of (a) two neighboring grafted chains and definition of the limiting distance *d*, (b) reactive polymer attached to substrate, and (c) movement of the functional groups of the reactive polymer in the direction of the end-functional groups of the grafting macromolecules.

themselves within the first monolayer in order to expose the terminal groups to the surface functionalities. This phenomenon ought to extend the duration of the first regime of grafting, leading to more efficient chain anchoring. For the reactions from a melt, the second and slower stage should start when practically all macromolecules that initially have physical contact with the surface are grafted. Namely, the (dry) thickness of the grafted layer should surpass $2R_g$ before the second regime comes into effect. Experimental data obtained for the grafting from the melt suggested that, indeed, the amount of material attached from the melt was distinctly higher than the anchoring level observed for the grafting from a good solvent.[1,12,24] However, the $2R_g$ level was observed only on a few occasions and was not exceeded even with larger grafting times. The results implied that some additional factors prevented the chain addition at higher levels.

Luzinov et al.[24] studied grafting of carboxy-terminated polystyrene from a melt onto silicon substrates modified with epoxysilane (ES) monolayer. Comparison between the concentration of epoxy groups present initially on the surface (2 groups/nm^2) and the maximum density of the grafted chains (0.22 chains/nm^2) revealed that the number of sites available for the grafting was not a limiting factor for the chain attachment. It has been proposed that grafting from melt may be controlled by steric constraints through the limiting free volume between the grafted molecules that can be accessed by the late-arriving polymer chain. A simple geometrical model was discussed that adequately described observed experimental phenomena (Figure 1a). It was suggested that the limiting free volume can be characterized by the distance between the surface and intersection point of neighboring overlapped grafted macromolecules, *d* (Figure 1a). Indeed, this volume correlated with the size of the monomeric unit and varied little with the molecular weight of the chains being grafted.

In the present work, we report a novel procedure that allowed a significant increase in the number of end-functionalized macromolecules per area unit attached by the "grafting to" method. Dense and homogeneous grafted polymer layers were anchored from the melt onto a silicon wafer modified with a macromolecular anchoring layer rich in epoxy functional groups. Carboxylic acid- and anhydride-terminated polystyrenes (PS) were used for the grafting. A monolayer, of poly(glycidyl methacrylate) (PGMA) attached to silicon wafers, served as a macromolecular anchoring layer.

Experimental Section

ACS grade toluene and methyl ethyl ketone (MEK) were obtained from Acros Organics and were used as received. Dodecylamine (DA) from Aldrich was used as received. Highly polished single-crystal silicon wafers of {100} orientation (Semiconductor Processing Co.) were used as substrates. The substrates were first cleaned in an ultrasonic bath for 30 min, placed in a hot piranha solution (3:1 concentrated sulfuric acid/acid/30% hydrogen peroxide) for 1 h, and then rinsed several times with high-purity water. After being rinsed, the substrates were dried under a stream of dry nitrogen in clean room 100 conditions.

Glycidyl methacrylate from Aldrich was polymerized radically to give PGMA, $M_n = 24\,000$ g/mol, PDI = 1.7 (GPC). The polymerization was carried out in methyl ethyl ketone (MEK) from VWR at 60 °C. AIBN from Aldrich was used as an initiator. The polymer obtained was purified by multiple precipitations from MEK solution in diethyl ether. PGMA was dip-coated (Mayer Fientechnik D-3400) from 0.02 wt % MEK solution. The lower and the upper limits of the dip-coater were set to enable complete dipping of the substrate. The thickness of the macromolecular anchoring layer was 1 ± 0.1 nm as measured by ellipsometry.

Carboxy-terminated polystyrenes of different molecular weights from 4500 to 672 000 were obtained from Polymer Source, Inc. ($M_n = 45\,900$ and 672 000 g/mol) and Aldrich ($M_n = 143\,000$ g/mol) or synthesized by "living" free radical polymerization (M_n = 4500, 16 900, and 28 500 g/mol). All samples possessed a relatively narrow molecular weight distribution with M_w/M_n in the range 1.05−1.4. Aliphatic acid-terminated PS ($M_n = 28\,500$ g/mol) has been prepared by the TEMPO method under conditions similar to those described by Baumert et al.[26] 1.2 mol of styrene was heated together with 3.3 mmol of TEMPO and 3.3 mmol of 4,4′-azobis(4-cyanopentanoic acid) to 130° C for 24 h. 0.1 g of camphersulfonic acid was added to the system in order to accelerate the rate of polymerization and to reduce the autopolymerization reaction of styrene.[27] To avoid any unwanted side reaction during the sample preparation, the TEMPO group was removed by oxidation with *m*-chloroperbenzoic acid.[28] As initiator for the atom transfer radical polymerization (ATRP) 4-(1-bromoethyl)benzoic acid has been used, resulting in benzoic acid-terminated PS ($M_n = 4500$ and 16 900 g/mol).[29] The polymerization was catalyzed by 2,2′-bipyridine and CuBr and carried out at 130° C. In an analogous manner, a phthalic anhydride-terminated PS was synthesized using 4-(bromomethyl)phthalic anhydride as initiator (M_n = 11 900 g/mol, M_w/M_n = 1 0.42).

The initial polystyrene film was dip-coated from 0.7 wt % toluene solution onto wafers modified with a PGMA anchoring layer. The thickness of these polystyrene films, measured by ellipsometry, was 40 ± 5 nm. The specimens were annealed in a vacuum oven preheated to 150 °C to enable the end groups to react with the epoxy modified substrate. At high temperature, carboxylic groups are able to react with the epoxy groups of PGMA.[30] The grafting time was limited to 18 h, in view of

the fact that the previous investigation showed no significant changes at longer times.[24] In addition, a significant increase of grafting time beyond several days would increase the chances for local thermal destruction. The unbonded polymer was removed by multiple washing with toluene, including washing in an ultrasonic bath.

Ellipsometry was performed with a COMPEL discrete polarization modulation automatic ellipsometer (InOmTech, Inc.) at an incidence angle of 70°. A four-layer model (silicon substrate + silicon oxide layer + PGMA anchoring layer + polymer layer) was used to simulate experimental data. The refractive indices used to calculate the thickness of PGMA and polystyrene layers were 1.525 (calculated according to Van Krevelen[31]) and 1.59,[32] respectively. Original silicon wafers from the same batch and silicon wafers with a PGMA anchoring layer were tested independently and were used as reference samples for the analysis of grafted polymer layers. Scanning probe microscopy (SPM) studies were performed on a Dimension 3100 (Digital Instruments, Inc.) microscope. Tapping mode was used here to study the morphology of these films in ambient air. Silicon tips with a spring constant of 50 N/m were used to scan surfaces. Imaging was done at scanning rates in the range of 1−2 Hz. (After scanning the area of interest the samples were visualized with tapping mode by zooming out the scanned area to ensure that substrate was not damaged during the imaging.) The root-mean-square (RMS) roughness of our samples was evaluated from the SPM images recorded. RMS roughness is the standard deviation of feature height (Z) values within a given area:[33]

$$\text{roughness} = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - Z_{\text{ave}})^2}{N}} \tag{1}$$

where Z_{ave} is the average Z value within the given area, Z_i is the current Z value, and N is the number of points within a given area.

To characterize the polymer layers, several parameters have been evaluated.[34] The surface coverage (adsorbed amount), Γ (mg/m^2), was calculated from the ellipsometry thickness of the layer, h (nm), by the following equation:

$$\Gamma = h\rho \tag{2}$$

where ρ is the density of attached macromolecules. The density of PGMA (1.08 g/cm^3) was assumed to be the same as for poly(propyl methacrylate).[31] The density of PS used in our calculations was 1.05 g/cm^3.[31]

The chain density, Σ (chain/nm^2), i.e., the inverse of the average area per adsorbed chain, was determined by

$$\Sigma = \Gamma N_{\text{A}} \times 10^{-21}/M_{\text{n}} = (6.023\Gamma \times 100)/M_{\text{n}} \tag{3}$$

where N_{A} is Avogadro's number and M_{n} (g/mol) is the number-average molar mass of the grafted polymer.

The distance between grafting sites, D (nm), was calculated using the following equation:

$$D = (4/\pi\Sigma)^{1/2} \tag{4}$$

The free energy of mixing (ΔG_{M}), and thus miscibility, was estimated for the PS/PGMA pair by the Flory−Huggins equation:[35]

$$\frac{\Delta G_{\text{M}}}{V_0 KT} = \frac{\nu_1\nu_2\chi}{V_x} + \frac{\nu_1 \ln \nu_2}{V_1} + \frac{\nu_2 \ln \nu_1}{V_2} \tag{5}$$

where ν_1 and ν_2 are volume fractions of two components, V_1 and V_2 are volumes per polymer molecule, K is Boltzmann's constant, V_0 is the volume occupied by N_0 number of cells in Flory−Huggins theory (taken as 1 cm^3), and V_x is given by[35]

$$\frac{1}{V_x} = \left(1 - \frac{2}{Z}\right)/V_{\text{R}} \tag{6}$$

where Z is the lattice coordination number, ranging from 6 to 12, and V_{R} is the volume occupied by a monomer unit. In our calculations the geometrical mean of PS and PGMA monomer unit's volumes and $Z = 10$ were used.

The interaction parameter, χ, for the PS/PGMA pair was estimated by use of the following equation:[35]

$$\chi = \frac{V_{\text{r}}(\delta_1 - \delta_2)^2}{RT} \tag{7}$$

where V_{r} is the molar volume of monomer unit of the polymer, δ_1 and δ_2 are the solubility parameters of PS and PGMA, R is the universal gas constant, and T is the temperature in kelvin. The geometrical mean of V_{r} for the PS and PGMA monomer units was used. Here the solubility parameters were estimated using the atomic increments approach proposed by Askadskii.[36] Calculated values of the solubility parameter are 18.65 and 20.49 (J/cm^3)$^{1/2}$ for PS and PGMA, respectively.

The interphase thickness was approximated by the following equation:[37]

$$S_{\text{th}} = \frac{2a}{\sqrt{6\left(\chi - \left(\frac{1}{N_1} + \frac{1}{N_2}\right)2 \ln 2\right)}} \tag{8}$$

where a is the statistical segment length and N_1 and N_2 are the degrees of polymerization of two polymers ($N_2 = 169$ (PGMA)). The statistical segment length for PGMA and PS was assumed to be 0.6 nm.[35]

Results and Discussion

Macromolecular Anchoring Layer Approach. There are two common approaches for the attachment of polymeric chains by the grafting to method. The first one involves the formation of a monolayer consisting of functional groups (e.g., epoxy, amino, or hydroxy) active toward terminally functionalized polymer.[24,38,39] A different approach relies on the reactions between end-functionalized chains and native functional groups originally present on the substrate surface.[8,11,12] Silane, thiol, and epoxy chemistries have proved to be suitable for the grafting in this case. A common feature of the two approaches is a restricted mobility of the functional groups located on the surface. As a result, at higher grafting densities the screened reactive groups cannot be reached by the end functionalities of the macromolecules being attached.

An alternative method for synthesis of the grafted polymer layers involves a primary polymer (mono)layer, active toward both surface and end-functionalized macromolecules. The primary polymer (mono)layer can be prepared from linear[40−42] or hyperbranched[43,44] macromolecules. The polymer is used for the initial surface modification as well as generation of the highly reactive anchoring layer (Figure 1b). When deposited on a substrate, the layer first reacts with the surface through formation of covalent bonds. The reactive units located in the "loops" and "tails" sections of the attached macromolecules are not connected to the surface.[45] These free groups offer the potential for the further modifications by chemical synthesis and serve as reactive sites for the subsequent attachment of the end-functionalized macromolecules. The major difference between this method of surface activation and the traditional self-assembled monolayer approach lies in the mobility of functional groups located in the loops

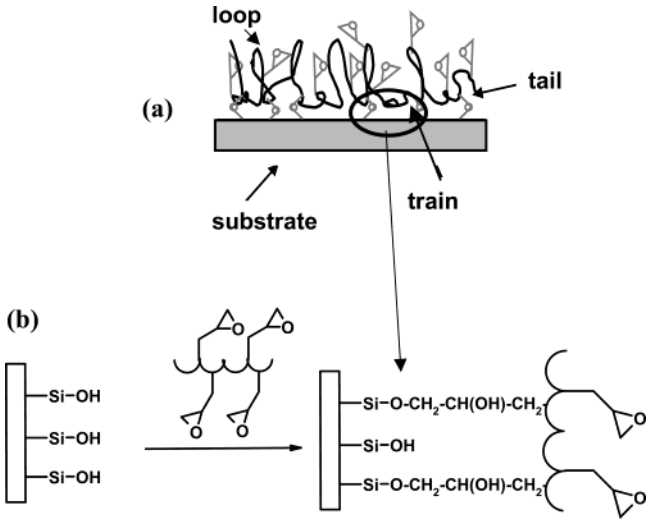

Figure 2. Schematic representation of (a) PGMA adsorbed on surface and (b) chemical bonding of the PGMA layer to the surface.

and tails of the adsorbed macromolecule. In fact, throughout the grafting, not only are the end-functional groups of attaching macromolecules migrating toward the surface located reactive sites but also the reactive sites may be moving in the direction of the end groups (Figure 1c).

PGMA Primary Layer. We used PGMA to form a reactive anchoring polymer layer. A polymer with epoxy functionality was chosen, since the reactions of epoxy groups are quite universal and can covalently anchor PGMA to the substrate surface.[40] The glycidyl methacrylate units located in the "loops" and "tails" sections of the attached PGMA chain were not connected to the substrate (Figure 2a). These free groups could serve as reactive sites for the subsequent attachment of PS macromolecules with complementary functional groups.

The silicon wafers coated with the PGMA layers (thickness 1 nm) were rinsed with a number of highly polar solvents including DMSO and THF. The layers could not be removed from the wafer by the solvent action, suggesting that PGMA was chemically bonded to the surface (Figure 2b).[40] SPM studies of PGMA layers revealed that the films were smooth and homogeneous. Figure 3a demonstrates that the PGMA layer uniformly covered the substrate surface on the microlevel. Morphology of the primary polymer layer on the nanolevel is shown in Figure 3b. The layer was molecularly flat with an RMS roughness at less than 0.3 nm.

During the grafting of PS to the PGMA layer at elevated temperature, beside reaction between carboxy groups of PS and epoxy functionalities of PGMA, self-cross-linking of the PGMA film may occur. The cross-linking reactions can reduce the surface concentration of the epoxy moieties available for the grafting. To study the degree of the deactivation, dodecylamine (DA) was attached to the ultrathin PGMA films. This low molecular weight substance was used as a probe for the presence of the accessible epoxy groups. The PGMA samples were preliminarily annealed at 120 °C in vacuo for different amounts of time to bring on the PGMA self-cross-linking. The amine attachment was carried out in warm (40 °C) toluene solution for 12−16 h. The extent of the DA grafting was measured by ellipsometry. The experiment demonstrated that approximately 40% of

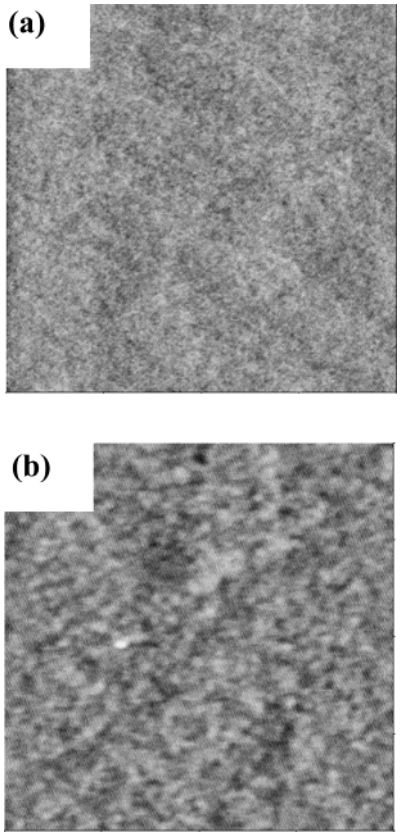

Figure 3. SPM topography images of PGMA primary monolayer deposited on the silicon wafer: (a) 10 × 10 μm; (b) 1 × 1 μm. Vertical scale: (a) 10 nm; (b) 5 nm.

epoxy groups were still available for the DA attachment after 4 h of annealing. The drop in initial activity of the adsorbed PGMA toward the DA anchoring occurred almost immediately after the sample was heated.

Grafting Capacity of PGMA Layers. The adsorbed concentration, Γ, of PGMA, constituting a layer of 1 nm thickness, was 1.08 mg/m^2. This corresponds to 0.027 PGMA chains/nm^2 or 4.5 epoxy groups/nm^2. The value of 4.5 epoxy groups/nm^2 represents the upper bound for the surface concentration of the epoxy functionalities. There is no doubt that the fraction of these groups responsible for the PGMA attachment to the surface was located in the train sections of the adsorbed chain. These glycidyl methacrylate units, as well as the units involved in the PGMA self-cross-linking during the grafting, are not available for the attachment reactions. According to Fleer et al.,[45] the train fraction for relatively high molecular weight polymer adsorbed on the surface is about 0.15−0.25. Additionally, a maximum of 60% of the epoxy groups in the loops and tails may be lost due to self-cross-linking. Therefore, we estimate that the PGMA layer used in this work had a surface concentration of active epoxy groups offered for the grafting at not less than 1.3 groups/nm^2. This (lower bound) value was comparable with the surface concentration previously reported for an ES monolayer (maximum 2 epoxy groups/nm^2).[24]

When end-functionalized polymer is grafted from the melt to a surface modified with the primary anchoring layer, interdiffusion phenomena have to be considered.[46] Typically, interpenetration at the interface may range from a depth of several angstroms to several nanometers, depending on the statistical segment length, the degree of polymerization, and the interaction parameter

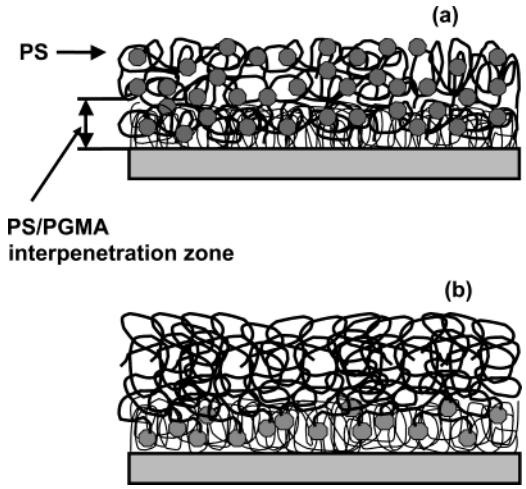

Figure 4. Schematic representation of (a) formation of PS/PGMA interpenetration zone and (b) grafting at different levels.

χ. If the interpenetration is minute, the grafting chains can access only glycidyl methacrylate units located at the surface of the PGMA films. Opposite, and more favorable for the grafting situation, is when the PS completely penetrates into PGMA film. Then, virtually all epoxy groups (that are not attached to the surface or lost due to cross-linking) are available for the reaction.

The thermodynamical miscibility for PGMA/PS pair at the grafting temperature used in the present study (150 °C) was estimated by eq 5 for different molecular weights of PS. The calculations revealed that $\Delta G_M > 0$ in our experimental conditions, and consequently, there is no thermodynamical miscibility even for PS possessing the lowest molecular weight. Thus, when PGMA and PS are in contact, the interdiffusion zone has to be formed. The extent of interpenetration at the interface (or width of PS/PGMA interphase) was approximated by eq 8. According to the estimations, the extent of interpenetration of PS in PGMA varied from 1.8 nm for PS possessing the lowest molecular weight (4500 g/mol) to 1.5 nm for PS with the highest M_n (672 000 g/mol). Thus, PS has to penetrate extensively inside the PGMA layer possessing a thickness of 1 nm. The random diffusion of PS molecules into the PGMA layer leads to formation of a complex surface with fractal characteristics.[47] This process increases the dimensionality of the PGMA film (to $d > 2$) compared to that of a functional self-assembled monolayer deposited on silicon wafer. In this scenario, the epoxy functional groups positioned inside the primary anchoring layer are available for the grafting. The reactive epoxy units located in the tails and loops of the adsorbed PGMA macromolecules can migrate in the direction of the end groups (Figure 4a). Accordingly, grafting at different levels offers higher grafting density (Figure 4b).

It is necessary to mention that the miscibility and interphase equations, applied in the present study, have been developed for polymer chains in contact that are free to move and explore space with their entire contours. Therefore, the estimations by eqs 5 and 8 can be considered only as rough estimations in our case, since the adsorbed macromolecules are much more restricted in their movements. On the other hand, the adsorbed polymer chain consists of the trains, loops, and tails of particular length. And the number of monomeric units in the loops and tails pinned to the surface by trains is much lower than the degree of polymerization of the adsorbed macromolecule. Thus, it may be essential to consider contact between the loops and tails of PGMA with penetrating PS molecules and not the contact of PS with the entire PGMA chain. The loops and tails possessing lower molecular weight may perhaps form a more extended interphase with PS and even appear to be miscible with the penetrating chains.

PS Grafting to Primary Polymer Layer. To highlight features and distinctions of the grafting to the macromolecular anchoring layer, results on the PS grafting to the layer were compared with those found in a study on PS grafting to the ES monolayer deposited on silicon wafer.[24] For this purpose, we have used the same PS samples and experimental procedure for the grafting and sample treatments. An attempt was made to conduct direct comparison between grafting to the functional self-assembled monolayer with restricted mobility of the reactive sites and the grafting to a macromolecular monolayer that possessed the same reactive sites, but in which the sites are capable of migrating toward the end functional groups of the chains being grafted.

Figure 5 presents topographical images of high, medium, and low molecular weight polystyrene layers grafted to the macromolecular anchoring layer at 150 °C. For all molecular weights, anchored polystyrene chains homogeneously covered the substrate and possessed very fine surface texture. The PS grafted layer did not dewet at high temperature or desorb in a good solvent under ultrasonic treatment. RMS roughness was 0.4 ± 0.15 nm within a $1 \times 1\ \mu m^2$ area for all polymers grafted to the PGMA anchoring layer, while it was 0.25 ± 0.05 nm for all polymers grafted to the ES monolayer (Figure 6). The increase in the surface corrugation can be attributed to the formation of the segmental interdiffusion zone between PS chains being grafted and loops/tails of adsorbed PGMA (Figure 4).

The surface coverage, Γ, initially increases for the range $43 < N < 440$ (N is the degree of polymerization), passes through a maximum at $N = 440$, and then decreases (Figure 7a). This trend is in good agreement with that obtained for grafting to the ES self-assembled monolayer. The maximum is close to the critical entanglement molecular weight of PS, M_C, which is 31 200 g/mol ($N_C = 300$).[47] However, it is necessary to stress that the surface coverage and hence the thickness of the PS grafted to PGMA layer are 2−3-fold greater than those obtained for the ES monolayer. The observed result demonstrates that increased mobility of the reactive groups located in tails/loops sections of the adsorbed PGMA does cause the significant increase in the grafting efficiency. Accordingly, higher grafting density was reached when PGMA primary layer was employed for the grafting (Figure 7b).

Figure 8 shows how the distance between grafting sites (D), reduced to twice the radius of gyration for the PS macromolecule ($2R_g$), varies with the degree of polymerization of the grafted polymer. R_g for the PS macromolecules was calculated from the following equation:[24]

$$R_g = a(N/6)^{1/2} \tag{9}$$

The dependence demonstrates minima for intermediate molecular weights of PS in the cases of PGMA and ES.

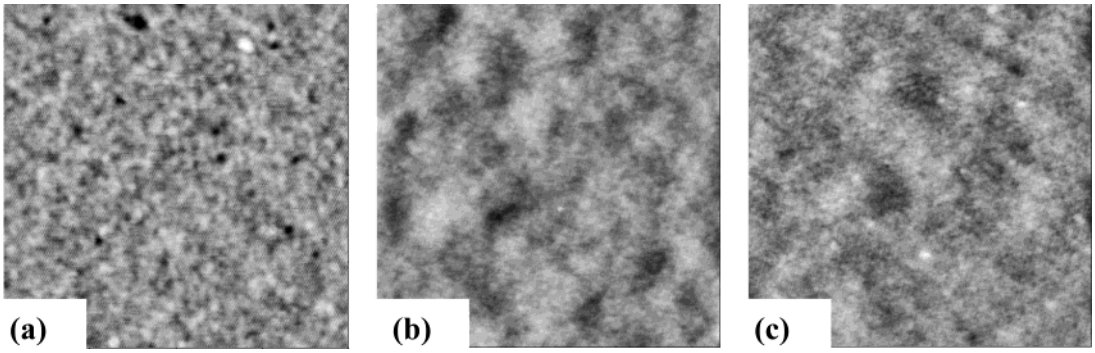

Figure 5. SPM topographical images ($1 \times 1\ \mu$m) of grafted PS layers possessing different molecular weights (a) 4500, (b) 45 800, and (c) 672 000 g/mol grafted to 1 nm PGMA layer. Vertical scale: 10 nm.

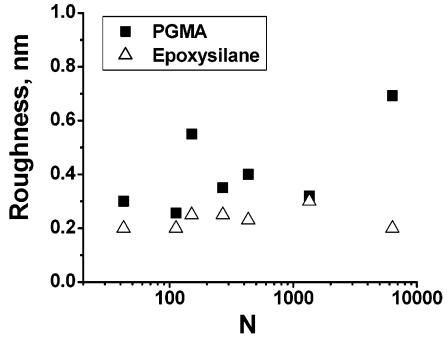

Figure 6. Roughness of the grafted layers vs degree of polymerization (N) of grafted PS chains. (Data for ES monolayer are taken from ref 24.)

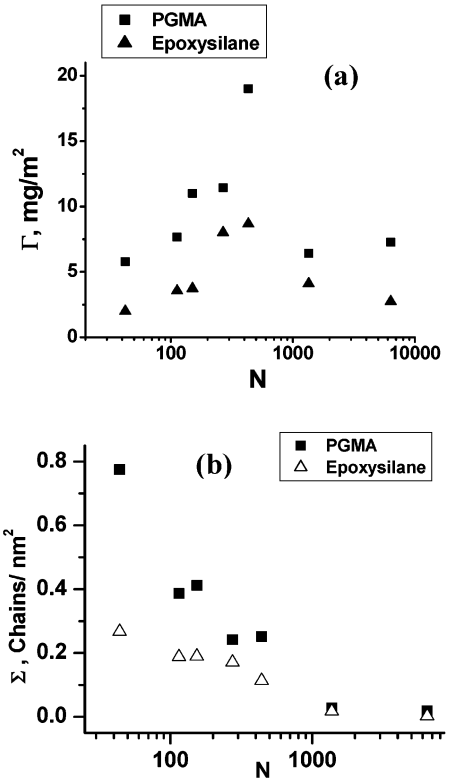

Figure 7. (a) Surface coverage, Γ (mg/m^2), and (b) grafting density, Σ (chains/nm^2), vs degree of polymerization (N) of grafted PS chains. (Data for ES monolayer are taken from ref 24.)

The minimum corresponds to M_C of PS, which confirms highest grafting density at $M_n \approx M_C$. The decrease in grafting density for $M_n > M_C$ can be attributed to the very low rate of interfacial reaction for high molecular weight polymers due to slow diffusion/reorientation of the entangled chains.[48−50] For polymers with $M_n > M_C$, the reaction rate constant decreases by several orders of magnitude, due to which the reactive ends become kinetically trapped within the limited distance from the surface. This prevents a high grafting density for the grafting time of 18 h under investigation.

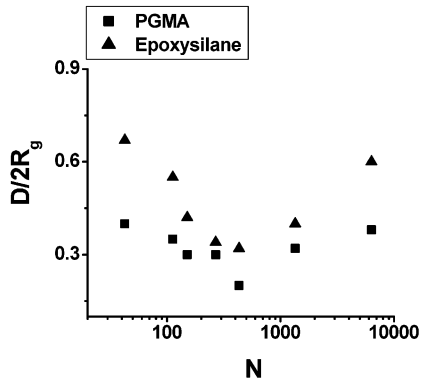

Figure 8. Distance between grafting sites (D) reduced to $2R_g$ vs degree of polymerization (N) of grafted PS chains. (Data for ES monolayer are taken from ref 24.)

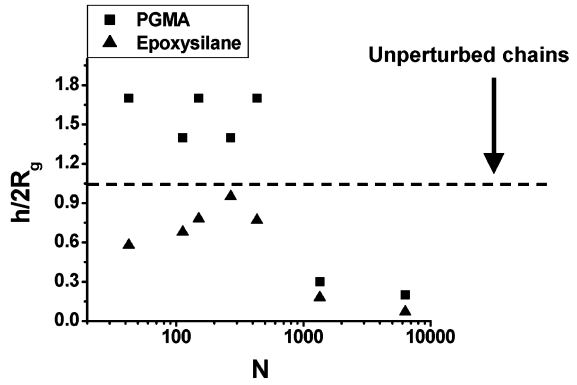

Figure 9. Height of the grafted layer (h) reduced to $2R_g$ vs degree of polymerization (N) of grafted PS chains. (Data for ES monolayer are taken from ref 24.)

The ratio of ellipsometry thickness, h, to $2R_g$ ($h/2R_g$) can be considered as a measure of chain stretching within the grafted layer. Figure 9 shows that the grafted layers are somewhat squashed along the surface normal for all molecular weights of PS grafted to the ES monolayer. In the case of polymers grafted to the PGMA-modified surface the PS chains are significantly stretched for $M_n < M_C$. Actually, owing to the high density of attachment, the macromolecules expanded well beyond the unperturbed coil dimensions ($2R_g$).

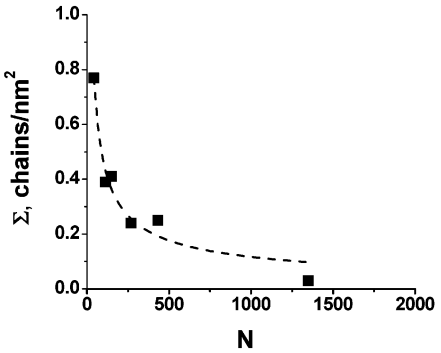

Figure 10. Grafting density (Σ) vs degree of polymerization (N) of grafted PS chains.

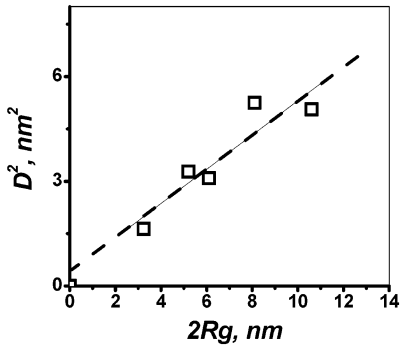

Figure 11. Distance between grafting sites (D) vs chain dimension ($2R_g$).

However, the grafted layers synthesized from the macromolecules possessing high molecular weight are still compressed along the surface normal. It was observed for the ES system[24] that a nonlinear function of the type $\Sigma \propto N^{-\delta}$ gives a reasonable description of the experimental grafting data. The parameter δ was in the range 0.4−0.6. Figure 10 shows that indeed $\delta = 0.6$ also gives a reasonable fit for the current experimental data on the grafting to a PGMA anchoring layer.

Comparison of the results, for the grafting to the PGMA primary layer with earlier data collected for the ES monolayer, suggests that there are more similarities than differences between those grafting processes. The same major trends were observed. However, the grafting to the PGMA monolayer was much more effective. It revealed that the reactive epoxy units located in the tails and loops of the adsorbed PGMA are more accessible than the reactive sites of ES monolayer. Thus, steric constrains in between two grafted chains, which may prevent grafting of additional chain end, turn out to be less pronounced in the PGMA case.

In the framework of the simple model proposed in ref 24 (Figure 1a), an increase of the degree of overlapping (decrease of D) effectively leads to increased "screening" of the surrounding surface. From geometrical consideration, the following relationship was obtained:

$$D^2 = 4d(2R_g) - 4d^2 \qquad (10)$$

which is valid for $R_g > 2d$. In the course of the grafting, the distance between the anchored chains decreases to the level at which the segments with the restricted mobility overlap. The mobility of these segments is limited, since they or their neighbors are chemically connected to the surface. At such a critical distance, the surface becomes screened, and there is not enough free volume in the vicinity of the interface for another segment to access a binding site. It was suggested that the limiting free volume could be characterized by the distance between the surface and the intersection point of neighboring overlapped grafted macromolecules, d, in their unperturbed state. By plotting D^2 vs $2R_g$, the critical distance d can be estimated.

Figure 11 shows the D^2 against $2R_g$ dependence for the PS layers grafted to the PGMA adsorbed on the surface. Only data for the polymers with molecular weight close to and lower than M_C were used for the correlation, since the grafting definitely approached equilibrium in this case. Indeed, the dependence was virtually a linear fit. The slope of the fit corresponded to $d = 0.13$. The slope for the grafted layers on an ES modified surface gave $d = 0.23$. The lower d value for the PGMA system confirmed that the macromolecular anchoring layer made the epoxy sites more accessible to the end-functional groups of the polystyrene chains.

Conclusions

Dense and homogeneous grafted polymer layers were permanently anchored from the melt onto a silicon wafer modified with the PGMA anchoring layer. The glycidyl methacrylate units located in the loops and tails sections of the attached PGMA chain were not connected to the substrate and served as reactive sites for the subsequent attachment of PS macromolecules with a carboxyl functional group. The grafted layers did not dewet at elevated temperatures and did not desorb in a good solvent under ultrasonic treatment. Comparison of the results for the grafting to the PGMA primary layer with published data obtained for the ES monolayer suggests that there are many similarities between these grafting processes. The same major trends were observed. However, the grafting to the PGMA layer was much more effective. It appears that the epoxy groups located in the loops/tails of the adsorbed PGMA macromolecule are more accessible to the end-functional groups of polystyrene when compared to ES with terminal epoxy groups located mainly at the monolayer surface. It is the author's determination that the high efficiency of PGMA in the grafting reactions is related to the high mobility of the epoxy reactive groups and to the formation of an interpenetrating zone at the PS/PGMA interface.

Acknowledgment. This work was supported by the Department of Commerce through the National Textile Center, Grant M01-CL03, and in part by the ERC Program of the National Science Foundation under Award EEC-9731680. The authors thank Dr. J. R. Aspland, Dr. V. Gorbunov, Dr. S. S. Minko, and Dr. V. V. Tsukruk for helpful discussions and Dr. V. Klep for important advice and the synthesis of PGMA.

References and Notes

(1) Norton, L. J.; Smigiova, V.; Pralle, M. U.; Hubenko, A.; Dai, K. H.; Kramer, E. J.; Hahn, S.; Begrlund, C.; DeKoven, B. *Macromolecules* **1995**, *28*, 1999.
(2) Inoue, H.; Uyama, Y.; Uchida, E.; Ikada, Y. *Cell Mater.* **1992**, *2*, 21.
(3) Luzinov, I.; Minko, S.; Senkovsky, V.; Voronov, A.; Hild, S.; Marti, O.; Wilke, W. *Macromolecules* **1998**, *31*, 3945.
(4) Ruckert, D.; Gueskens, G. *Eur. Polym. J.* **1996**, *32*, 201.
(5) Tomita, N.; Tamai, S.; Okajima, E.; Hirao, Y.; Ikeuch, K.; Ikada, Y. *J. Appl. Biomater.* **1994**, *5*, 175.
(6) Ruckenstein, E.; Chang, D. B. *J. Colloid Interface Sci.* **1988**, *123*, 170.

(7) Leermakers, F. A. M.; Zhulina, E. B.; van Male, J.; Mercurieva, A. A.; Fleer, G. J.; Birshtein, T. M. *Langmuir* **2001**, *17*, 4459.
(8) Zhao, B.; Brittain, W. J. *Prog. Polym. Sci.* **2000**, *25*, 677.
(9) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983. de Gennes, P.-J. *Macromolecules* **1980**, *13*, 1069.
(10) Milner, S.; Witten, T.; Cates, M. *Macromolecules* **1988**, *21*, 2610. Solis, F. J.; Tang, H. *Macromolecules* **1996**, *29*, 7953.
(11) Karim, A.; Tsukruk, V. V.; Douglas, J. F.; Satija, S. K.; Fetters, L. J.; Reneker, D. H.; Foster, M. D. *J. Phys. II* **1995**, *5*, 1441.
(12) Jones, R. A. L.; Lehnert, R. J.; Schonerr, H.; Vancso, J. *Polymer* **1999**, *40*, 525.
(13) Auroy, P.; Auvray, L.; Leger, L. *Macromolecules* **1991**, *24*, 5158.
(14) Clarke, C. J.; Jones, R. A. L.; Clough, A. S. *Polymer* **1996**, *37*, 3813.
(15) Clarke, C. J. *Polymer* **1996**, *37*, 4747.
(16) Jordan, R.; Ulman, A.; Kang, J. F.; Rafailovich, M. H.; Sokolov, J. *J. Am. Chem. Soc.* **1999**, *121*, 1016.
(17) Guzonas, D. A.; Boils, D.; Tripp, C. P.; Hair, M. L. *Macromolecules* **1992**, *25*, 2434. Johner, A.; Joanny, J. F. *Macromolecules* **1990**, *23*, 5299. Marques, C. M.; Joanny, J. F. *Macromolecules* **1989**, *22*, 1454.
(18) Clarke, C. J.; Jones, R. A. L.; Edwards, J. L.; Shull, K. R.; Penfold, J. *Macromolecules* **1995**, *28*, 2042.
(19) Tsubokawa, N.; Satoh, M. *J. Appl. Polym. Sci.* **1997**, *65*, 2165.
(20) Prucker, O.; Rühe, J. *Langmuir* **1998**, *14*, 6893.
(21) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. J. *Science* **1999**, *121*, 3557.
(22) Wittmer, J. P.; Cates, M. E.; Johner, A.; Turner, M. S. *Europhys. Lett.* **1996**, 397.
(23) Spange, S.; Simon, F.; Shütz, H.; Schramm, A.; Winkelmann, H. *J. Macromol. Sci., Chem.* **1992**, *A29*, 997. Jordan, R.; Ulman, A. *J. Am. Chem. Soc.* **1998**, *120.* Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716.
(24) Luzinov, I.; Julthongpiput, D.; Malz, H.; Pionteck, J.; Tsukruk, V. V. *Macromolecules* **2000**, *33*, 1043.
(25) Ligoure, C.; Leibler, L. *J. Phys. (Paris)* **1990**, *51*, 1313.
(26) Baumert, M.; Muelhaupt, R. *Macromol. Rapid Commun.* **1997**, *18*, 787.
(27) Georges, M. K.; Veregin, R. P. N.; Katzmaier, P. M.; Hamer, G. K.; Saban, M. *Macromolecules* **1994**, *27*, 7228.
(28) Malz, H.; Komber, H.; Voigt, D.; Pionteck, J. *Macromol. Chem. Phys.* **1998**, *199*, 583.
(29) Malz, H.; Komber, H.; Voigt, D.; Hopfe, I.; Pionteck, J. *Macromol. Chem. Phys.* **1999**, *200*, 642.
(30) Koning, C.; Van Duin, M.; Pagnoulle, C.; Jerome, R. *Prog. Polym. Sci.* **1998**, *23*, 707.
(31) Van Krevelen, D. W. *Properties of Polymers*; Elsevier: Amsterdam, 1997.
(32) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; John Wiley & Sons: New York, 1999.
(33) *Scanning Probe Microscopy: Training Notebook*; Digital Instruments, Veeco Metrology Group: Santa Barbara, CA, 2000; p 40.
(34) Henn, G.; Bucknall, D. G.; Stamm, M.; Vanhoorne, P.; Jerome, R. *Macromolecules* **1996**, *29*, 4305.
(35) Sperling, L. H. *Polymeric Multicomponent Materials;* John Wiley & Sons: New York, 1998.
(36) Askadskii, A. A. *Physical Properties of Polymers: Prediction and Control*; Gordon and Breach Publishers: Amsterdam, 1996.
(37) Broseta, D.; Fredrickson. G. H.; Helfand, E.; Leibler, L. *Macromolecules* **1990**, *23*, 132. Schubert, D. W.; Stamm, M. *Europhys. Lett.* **1996**, *35*, 419.
(38) Penn, L. S.; Hunter, T. F.; Lee, Y.; Quirk, R. P. *Macromolecules* **2000**, *33*, 1105.
(39) Tsukruk, V. V.; Luzinov, I.; Julthongpiput, D. *Langmuir* **1999**, *15*, 3029. Luzinov, I.; Julthongpiput, D.; Liebmann-Vinson, A.; Cragger, T.; Foster M. D.; Tsukruk, V. V. *Langmuir* **2000**, *16*, 504.
(40) Kothe, M.; Muller, M.; Simon, F.; Komber, H.; Jacobasch, H.-J.; Adler, H.-J. *Colloids Surf. A* **1999**, *154*, 75.
(41) Iyer, K. S.; Klep, V.; Luzinov, I. *Polym. Prepr.* **2002**, *43* (1), 455. Zdyrko, B.; Klep, V.; Luzinov, I. *Polym. Prepr.* **2002**, *43* (1), 586.
(42) Shibanova, O. B.; Medvedevskikh, Y. G.; Voronov, S. A.; Tokarev, V. S.; Stamm, M.; Antipov, E. M. *J. Polym. Sci., Ser. A* **2002**, *44*, 258.
(43) Sidorenko, A.; Zhai, X. W.; Simon, F.; Pleul, D.; Tsukruk, V. V. *Macromolecules* **2002**, *35*, 5131.
(44) Sidorenko, A.; Zhai, X. W.; Greco, A.; Tsukruk, V. V. *Langmuir* **2002**, *18*, 3408.
(45) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall: New York, 1993.
(46) Sperling, L. H. *Introduction to Physical Polymer Science*; John Wiley & Sons: New York, 2001.
(47) Wool, R. P. *Polymer Interfaces: Structure and Strength*; Hunser Publishers: Munich, 1995; p 102.
(48) O'Shaghnessy, B.; Sawhney, U. *Phys. Rev. Lett.* **1996**, *76*, 3444.
(49) O'Shaghnessy, B.; Sawhney, U. *Macromolecules* **1996**, *29*, 7230.
(50) Fredrickson, G. H. *Phys. Rev. Lett.* **1996**, *76*, 3440.

MA034460Z