Effect of Macromolecular Anchoring Layer Thickness and Molecular Weight on Polymer Grafting

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ABSTRACT: Carboxylic acid-terminated polystyrene (PS) of different molecular weights from 4500 to 672 000 was grafted from melt onto silicon substrates modified with a macromolecular anchoring layer. The study was focused on influence of thickness and molecular weight of the layer on the permanent attachment of the end-functionalized PS layers by the "grafting to" approach. Poly(glycidyl methacrylate) (PGMA) was used to form the reactive anchoring interface. The grafting trends observed and the amount of PS anchored were not significantly affected by the thickness and molecular weight of the anchoring layer, except for the case of lower molecular weight PS (4500 g/mol). The higher grafting in the latter case may be a result of formation of an extremely extended interphase between loops of the adsorbed PGMA and the low molecular weight PS.

Introduction

The modification of substrates by end-grafted polymer layers has attracted much industrial and academic interest.[1,2] Particular attention has been given to "polymer brushes" because of their unique behavior that can be easily modeled and interpreted.[3] Literally, if the distance between grafted chains is smaller than the end-to-end distance of a polymer chain, the layer of the grafted chains is in the regime of polymer brush.[4] In the brush regime, grafted chains are forced to stretch in the direction normal to the surface, and their conformation is determined by the energy balance between the elastic free energy of the stretched chain and the energy of interaction between the solvent and segments.[5] It is recognized that grafting of polymer brushes is an effective way to control surface properties such as adhesion,[6] wettability,[7,8] friction,[9] stabilization of colloids,[10] and cell protein interaction.[11]

Synthesis of the polymer brushes can be readily accomplished by a "grafting to" method.[1,12−14] In the "grafting to" technique, end-functionalized polymer molecules react with complementary functional groups located on the surface to form tethered chains. End-functionalized polymers (with a narrow molecular weight distribution) can be synthesized by living, anionic, cationic, radical, group transfer, and ring-opening metathesis polymerizations. Thus, the advantage of the method is that the well-defined end-functionalized polymers can be used for the grafting, and as a result, well-defined brushes can be readily obtained. The covalent bond formed between the polymer chain and the substrate makes the polymer brushes resistant to chemical environmental conditions. 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.[13,15] 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 polymer brush obtained typically has low grafting density and low thickness. The density of the brush obtained by the "grafting to" method can be increased if the macromolecules attachment is conducted from a solution at Θ conditions[12] or from melt.[13,16−18] Grafting from melt in particular offers potential advantages over grafting from solution, since the excluded-volume interactions that make it difficult for chains to penetrate an initial grafted layer are screened out in the melt.[13] If the grafting is carried out from the 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 themselves within the first monolayer in order to expose the terminal groups to the surface functionalities. Additional increase in grafting density for the attachment from the melt can be achieved when a macromolecular (primary) anchoring layer is used for the introduction of reactive group on a substrate surface. The primary polymer (mono)layer can be prepared from linear[19−21] or hyperbranched macromolecules.[22−24]

The grafting employing the primary layer was reported in details in our previous communication.[21] We studied attachment of end-functionalized polystyrene (PS) from melt to a 1 nm thick layer of poly(glycidyl methacrylate) (PGMA), attached to silicon wafers. In essence, the PGMA reactive polymer chains constituting the primary layer (when deposited on the surface) reacted with the surface through formation of covalent bonds. The functional groups located in the "loops" and "tails" sections of the attached macromolecule were not bound to the substrate while the functional groups in the "train" sections of the attached macromolecule were anchored to the substrate (Figure 1). The free groups in the "tails" and the " loops" of the macromolecule served as reactive sites for the subsequent anchoring of the end-functionalized polymers. Comparison of the results for the grafting to the PGMA primary layer with published data[16] obtained for the epoxysilane monolayer suggested 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. The epoxy groups located in the loops/tails of the adsorbed PGMA macromolecule were

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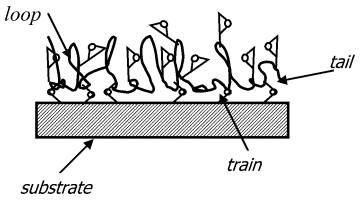

Figure 1. "Tail−train−loop" model of the macromolecular anchoring layer.

more accessible to the end-functional groups of polystyrene when compared to epoxysilane with terminal epoxy groups located mainly at the monolayer surface. It was concluded that the high efficiency of PGMA in the grafting reactions was related to the high mobility of the epoxy reactive groups and to the formation of an interpenetrating zone at the PS/PGMA interface. On the other hand, the query still remained if increasing the molecular weight and/or thickness of the PGMA layer would influence the reported grafting density.

To this end, the present study is focused on investigating the influence of thickness and molecular weight of the primary polymer layer on the permanent grafting of carboxy-terminated PS layers from melt. PGMA was used to form the reactive anchoring layer. The PGMA molecular weight and thickness of the reactive layer were varied to change the morphology of the interfacial layer. In the study PGMA of three different molecular weight ((M_n = 24 000, 84 000, and 140 000 g/mol) was employed. The thickness of the reactive layers (1−7 nm) was kept at the level below end-to-end distance for the polymer coils to ensure a monolayer formation.

Experimental Section

ACS grade toluene and methyl ethyl ketone (MEK) were obtained from Acros Organics and were 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/30% hydrogen peroxide) for 1 h, and then rinsed several times with high-purity water (18 MΩ cm, Nanopure). After being rinsed, the substrates were dried under a stream of dry nitrogen under clean room 100 conditions.

PGMA (M_n = 24 000, 84 000, and 140 000 g/mol) was synthesized by solution radical polymerization and purified by multiple precipitations. All the samples possessed molecular weight distribution of M_n/M_w in the range of 1.7−3.5. PGMA was deposited on the substrate by dip coating from 0.02, 0.05, 0.1, and 0.15 wt % MEK solutions to vary the thickness of the anchoring reactive layer. The lower and the upper limits of the dip coater (Mayer Fientechnik D-3400) were set to enable complete dipping of the substrate. The thickness of the macromolecular anchoring layer measured by ellipsometry was 1 ± 0.1, 2 ± 0.1, 4 ± 0.1, and 7 ± 0.4 nm, respectively.

Carboxy-terminated polystyrene of different molecular weights from 4500 to 672 000 were obtained from Polymer Source, Inc. (M_n = 45 900 and 672 000 g/mol) or Aldrich (M_n = 143 000 g/mol) and were synthesized by "living" free radical polymerization (M_n = 4500, 11 900, 16 900, and 28 500 g/mol) at IPF, Dresden, Germany. All the samples possessed a relatively narrow molecular weight distribution of M_n/M_w in the range of 1.05−1.4.

The initial PS film was dip-coated from 0.7 wt % toluene solution onto wafers modified by the PGMA anchoring layer. The thickness of these polystyrene films measured by ellipsometry was 40 ± 5 nm. The specimens were placed in a vacuum oven at 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.[25]

The grafting time was limited to 18 h as it was observed in the previous investigation[16] that no significant changes were observed beyond the first 18 h of grafting. In addition, significant increase of grafting time beyond several days would increase the chances for local thermal destruction. The unbounded polymer was removed by multiple washing with toluene, including washing in an ultrasonic bath.

Ellipsometry was performed with COMPEL discrete polarization modulation automatic ellipsometer (InOmTech, Inc.) at an angle of incidence 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 and 1.59, respectively. Original silicon wafers from the same batch and silicon wafers with 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. We used tapping mode to study the morphology of these films in ambient air. Silicon tips with spring constant of 50 N/m were used to scan surfaces. Imaging was done at scanning rates in the range of 1−2 Hz. Root-mean-square (rms) roughness of samples was evaluated from the recorded SPM images. The rms roughness is the standard deviation of feature height (Z) values within a given area:[26]

$$\mathrm{rms} = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - Z_{av})^2}{N}} \tag{1}$$

where Z_{av} 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 layer, several parameters have been evaluated.[27] The surface coverage, 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 density of PS (1.05 g/cm^3).[13] The density of PGMA (1.08 g/cm^3) was assumed to be close to poly(propyl methacrylate).[21]

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

$$\Sigma = \Gamma N_A \times 10^{-21}/M_n = (6.023\Gamma \times 100)/M_n \tag{3}$$

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 radius of gyration (R_g) and the end-to-end distance ($\langle r^2\rangle^{1/2}$) for the PS-COOH and PGMA macromolecules were estimated by the following equations:[27,28]

$$R_g = a(N/6)^{0.5} \tag{5}$$

$$\langle r^2\rangle^{1/2} = 6^{0.5}R_g \tag{6}$$

where N is the degree of polymerization and a is the statistical segment ($a \approx 0.6$ nm for PS);[28,29] the statistical segment for PGMA (0.6 nm) was assumed to be same as for poly(methyl methacrylate).[30]

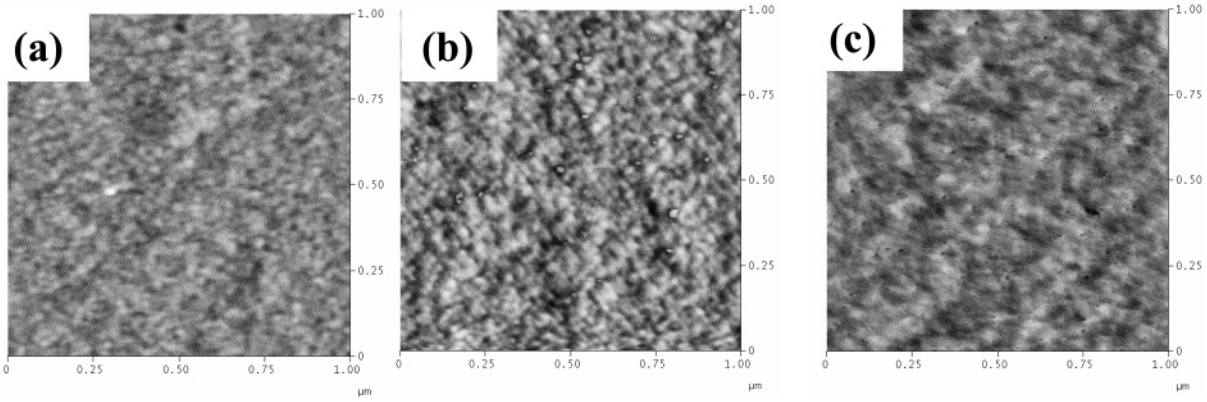

Figure 2. SPM 1 × 1 μm images of PGMA anchoring layer attached to a silicon substrate: (a) thickness (1 nm); (b) thickness (7 nm); (c) thickness (4 nm). Molecular weight: (a, b) 24 000 g/mol, (c) 140 000 g/mol. Vertical scale: (a, b, c) 5 nm.

The free energy of mixing (ΔG_M) was estimated for the PS/PGMA pair by the Flory−Huggins equation:[30]

$$\frac{\Delta G_M}{V_0 KT} = \frac{\nu_1 \nu_2 \chi}{V_X} + \frac{\nu_1 \ln \nu_1}{V_1} + \frac{\nu_2 \ln \nu_2}{V_2} \tag{7}$$

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[30]

$$\frac{1}{V_X} = \left(1 - \frac{2}{Z}\right)/V_R \tag{8}$$

where Z is the lattice coordination number ranging from 6 to 12 and V_R is the molar volume of the monomer unit of the polymer. In our calculations the geometrical mean of PS and PGMA monomer units' volumes and $Z = 10$ were used.

The interaction parameter, χ, for the PS/PGMA pair was estimated by the following equation:[30]

$$\chi = \frac{V_r(\delta_1 - \delta_2)^2}{RT} \tag{9}$$

where V_r is molar volume of monomer unit of the polymer, δ_1 and δ_2 are solubility parameters of PS and PGMA, R is the universal gas constant, and T is the temperature in kelvin. In our estimations geometrical mean of V_r for PS and PGMA monomer units was used. The solubility parameters were estimated using atomic increments approach proposed by Askadskii.[31] Calculated values of the solubility parameter were 18.65 and 20.49 (J/cm^3)$^{1/2}$ for PS and PGMA, respectively.

The extent of the interpenetration at the interface (or width of PS/PGMA interphase) was approximated by the following equation:[32]

$$S_{th} = \frac{2a}{\sqrt{6\left(\chi - \left(\frac{1}{N_1} + \frac{1}{N_2}\right)2 \ln 2\right)}} \tag{10}$$

where a is statistical segment length and N_1 and N_2 are the degree of polymerization of two polymers, PS and PGMA in the present case.

Results and Discussion

For our study we prepared two sets of the PGMA anchoring layers. For the first set we kept molecular weight of the polymer (24 000 g/mol, $\langle r^2 \rangle^{1/2} \approx 7$ nm) constant while the thickness of the monolayer was varied from 1 to 7 nm. The second set comprised of the primary layers possessing very similar thickness (approximately 4 nm). In this case molecular weight of the PGMA was varied. SPM studies of the PGMA layers revealed that the anchoring macromolecular layers were smooth and homogeneous for all thickness and molecular weights (Figure 2). The PGMA films were found to be uniform on both nano- and microscales. The average SPM roughness for all layers was found to be 0.2 ± 0.05 nm within 1 × 1 μm^2. The stable and homogeneous PGMA anchoring layers had active accessible epoxy functionalities.[21] These reactive groups provided the platform for grafting of different molecular weights PS-COOH.

Figure 3 shows topographical images of the PS brushes of different molecular weights grafted to the anchoring layers. The SPM analysis revealed that the grafted PS homogeneously covered all substrates. The grafted layer did not dewet at high temperature or detach in a good solvent under ultrasonic treatment. SPM roughness was 0.45 ± 0.2 nm within a 1 × 1 μm^2 area for all polymers grafted to different PGMA anchoring layer beside PS (4500 g/mol) grafted to the thicker (4−7 nm) PGMA film. The grafted layer in this case had roughness of 1.2 ± 0.5 nm. It may indicate that the lower molecular weight PS extensively penetrated into the anchoring layers, and the fractal nature of the diffusion front results in the rougher topography of the brushes.

In Figure 4 the surface coverage, Γ, is plotted vs the degree of polymerization (N) of the grafting polymer. In general, Γ initially increases with N and passes through a maximum at approximately $N = 440$. This pattern is not unique for the PGMA anchoring layer and is in agreement with the values for grafting of the end-functionalized PS to an epoxysilane self-assembled monolayer.[16,21] The maximum is close to the critical entanglement molecular weight of PS, M_C, which is 31 200 g/mol ($N_C = 300$).[33] We performed multiple experiments on all the molecular weights of PS grafted to different thickness and molecular weights of PGMA, and concurrent results were obtained. Obtained experimental data indicated that (beside PS with molecular weight of 4500 g/mol) thickness of the macromolecular anchoring layer and molecular weight of the reactive polymer constituting the layer do not have decisive influence on the amount of the polymer grafted. In fact, for three different molecular weights and four different thicknesses close amounts of the grafted polymer were observed. Calculated surface concentration of epoxy groups (epoxy groups/nm^2 = ΣN) in PGMA layers with thickness of 1, 2, 4, and 7 nm were 4.6, 9.2, 18.4, and 32.2 epoxy groups/nm^2, respectively. However, the same amount of the epoxy groups was accessible for the

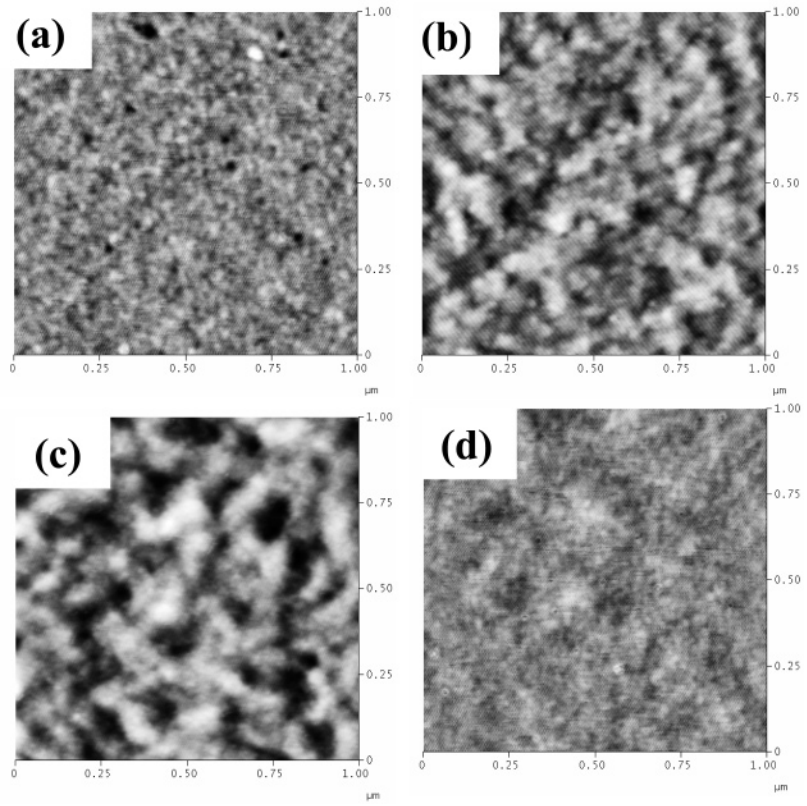

Figure 3. SPM 1 × 1 μm topography images of different molecular weights of polystyrene: (a−c) 4500 g/mol, (d) 143 000 g/mol grafted to (a) 1 nm and (b−d) 4 nm PGMA layer. Molecular weight of PGMA: (a, b) 24 000 g/mol; (c, d) 140 000 g/mol. Vertical scale: (a−d) 10 nm.

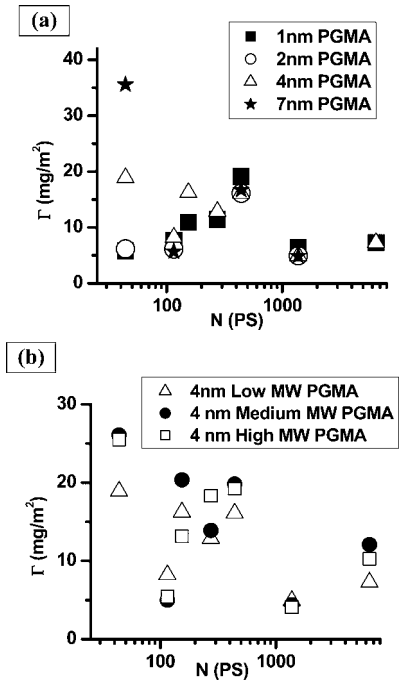

Figure 4. Surface coverage, Γ (mg/m^2), vs degree of polymerization (N) of polystyrene layers grafted to (a) 1, 2, 4, and 7 nm PGMA (24 000 g/mol) layers and to (b) 4 nm PGMA layers of different molecular weights 24 000, 84 000, and 140 000 g/mol.

grafting macromolecules of different molecular weight with the exception of the lowest molecular weight PS grafted to the thicker (4−7 nm) PGMA layers at much higher amounts (Figure 4a,b). It can also be concluded from Figure 5 that the number of PS chains per nm^2 (Σ) did not show significant change either with the increase in the thickness of the PGMA layer from 1 to 7 nm (Figure 5a) or with the increase in molecular weight of PGMA (Figure 5b), except for the case of PS (4500 g/mol).

It was observed in the earlier investigation[21] that a nonlinear function of the type $\Sigma \propto N^{-\delta}$ gave a reasonable description of the experimental grafting data. The parameter δ was in the range 0.4−0.6 for the data combined for the investigation on an epoxysilane monolayer[16] and those of Norton et al.[6] Figure 5c shows that indeed $\delta = 0.6$ gives a reasonable fit for the current experimental data. On the other hand, the unconventional grafting of PS (4500 g/mol) did not fit the nonlinear grafting density function. The above-mentioned deviations observed for the lower molecular weight PS are in a good agreement with SPM observations, where those samples demonstrated the higher roughness.

Figure 6 shows that the distance between grafting sites (D) reduced to 2 times the radius of gyration for the PS-COOH macromolecule ($2R_g$) varies with the degree of polymerization of the grafted polymer. (The lower molecular PS demonstrating atypical grafting behavior is not shown in Figure 6.) The dependence shows minima for intermediate molecular weights of polystyrene in both the cases (different thickness and different molecular weight of PGMA). The minimum corresponds to N_C of polystyrene, which confirms highest grafting density at $M_n \approx M_C$. This trend is in good agreement with that obtained earlier for grafting to thin (1 nm) PGMA layer[21] and an epoxysilane self-assembled monolayer.[16] The decrease in grafting density for $M_n > M_C$ was attributed to the very low rate of interfacial reaction for high molecular weight polymers due to slow

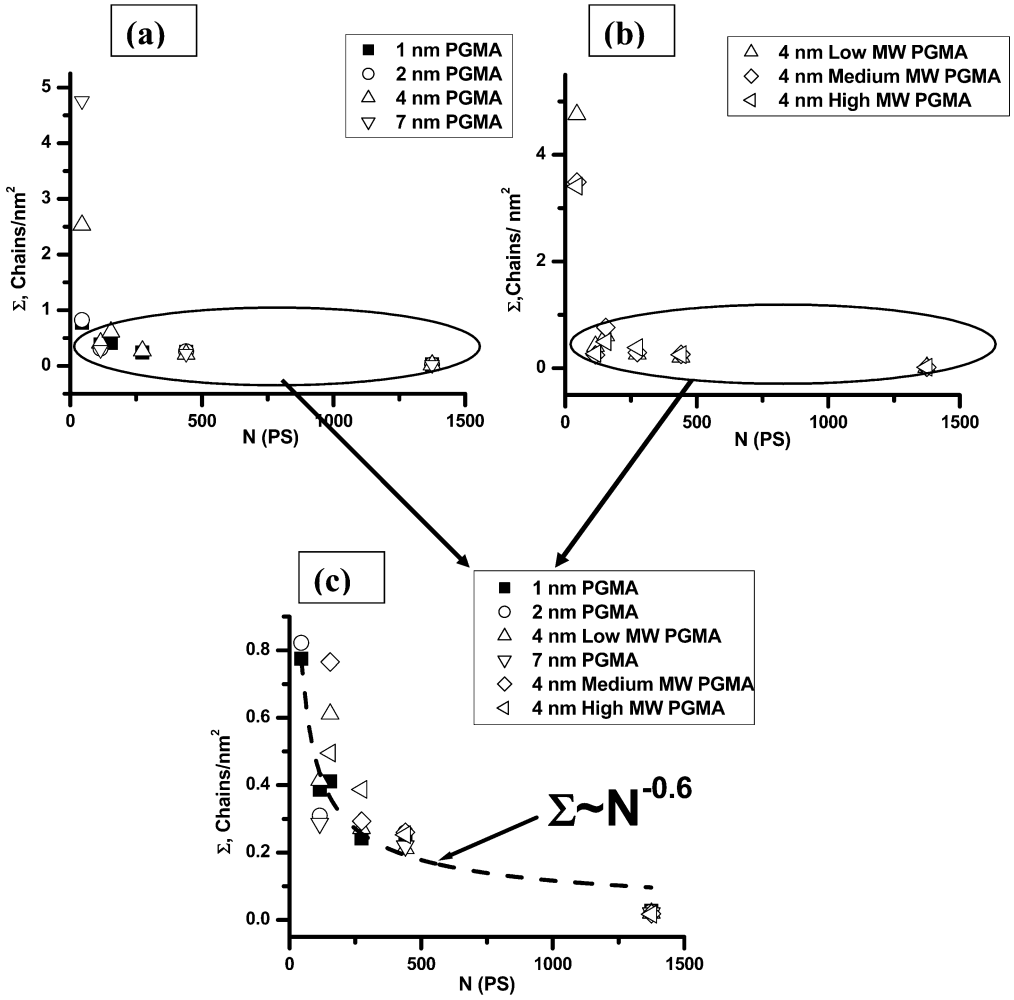

Figure 5. Grafting density (Σ) vs degree of polymerization (N) of polystyrene layers grafted to (a) 1, 2, 4, and 7 nm PGMA (24 000 g/mol) layers and to (b) 4 nm PGMA layers of different molecular weights 24 000, 84 000, and 140 000 g/mol.

diffusion of the entangled chains.[34,35] 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 dense grafting density for the grafting time of 18 h under investigation. The distance between the grafting sites did not vary for different thickness and molecular weights of PGMA.

The ratio of ellipsometry thickness, h, to $2R_g$ ($h/2R_g$) can be considered as a measure of the chain stretching within the dry layer. Figure 7 shows that in the case of polymers grafted to the PGMA modified surface the chains are stretched for polymers with $M_n \leq M_C$, while the chains are squashed for all high molecular weight polystyrenes. Thus, the accessible epoxy functional groups located in the "loops" sections of PGMA results in a densely grafted polymer layers for $M_n \leq M_C$, and because of the high grafting density, the chains are extended along the surface normal. While for higher molecular weight polymers, slow diffusion of the entangled chains prevents the denser grafting of PS and extensive stretching in the dry layer.

Review of the obtained experimental data certainly indicates that, when the higher molecular weight PS chains are considered, neither the thickness nor the molecular weight of PGMA has any decisive influence on the grafting of the end-functionalized PS to the macromolecular anchoring layer. Conversely, the lower molecular weight PS sample does not follow the trend, since significantly higher amounts of the polymer can be grafted to the thicker anchoring layers. The reasonable explanation of the observed results may involve polymer/polymer miscibility. Namely, the increase in the amount of PS (M_n = 4500 g/mol) grafted can be attributed to miscibility of the shorter chains with the PGMA chains constituting the primary layer. When the molecular weight increased, the miscibility is arrested and the thickness of the PGMA layer is not a parameter influencing the grafting. However, on the basis of the calculated ΔG_M (eq 7) for the PS/PGMA pair, it was evident that the free energy of mixing is positive for all the molecular weights of PS that have been used. The estimations suggested that PGMA and PS are not miscible. Thus, when PGMA and PS are in contact, the interdiffusion zone has to be formed. The extent of the interpenetration at the interface (or width of PS/PGMA interphase) was approximated by eq 10 and shown in Figure 8. According to the estimations, PS of different molecular weight has to penetrate to some extent (1.5−1.8 nm) inside the PGMA layer depending on the molecular weight. The estimations point out that the thickness of the anchoring film should not affect the grafting significantly. Thus, the interpenetration calculations failed to explain the grafting behavior of the lowest molecular weight PS.

Obviously, the interphase calculations developed for an immiscible polymer pair in contact could give only rough estimations for the penetration in the adsorbed

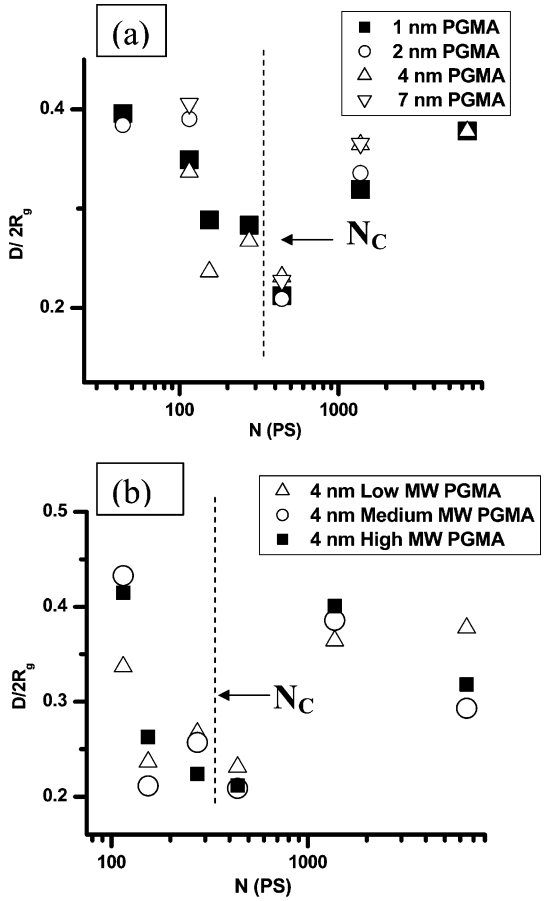

Figure 6. Distance between grafting sites (D) reduced to $2R_g$ vs degree of polymerization (N) of polystyrene layers grafted to (a) 1, 2, 4, and 7 nm PGMA (24 000 g/mol) layers and to (b) 4 nm PGMA layers of different molecular weights 24 000, 84 000, and 140 000 g/mol.

polymer layer. The adsorbed PGMA macromolecule in the anchoring layer could have three possible conformations (Figure 9): (a) single loop conformation (two pseudotails), (b) tail conformation, and (c) intermediate polydisperse pseudobrush conformation. The single loop conformation and the tail conformation have a very low probability of occurrence when compared to the polydisperse pseudobrush conformation. Hence, the PS chains are in contact with the loops and tails sections of the anchored PGMA polydisperse pseudobrush layer. These loops and tails can be assumed to behave like independent pseudomacromolecules forming a "Guiselin brush"[36] anchored to the substrate with degree of polymerization much lower than that of the entire PGMA molecule. The behavior in this case may be different when compared to the interaction of the PS chains with the whole PGMA chain.

ΔG_M was recalculated (employing eq 7) for the PS/PGMA−pseudobrush for various "loops" and "tails" sizes at different temperatures. (In the estimations we considered that loops and tails consist of the same amount of the monomeric units.) It is evident from Figure 10a that the shorter loops and tails of the adsorbed PGMA are predicted to be miscible with the PS chains. The PS chains of the higher molecular weight are miscible with tails and loops of size in the range of 6−9 glycidyl methacrylate units for the temperatures under consideration. Loops/tails of sizes up to 12 glycidyl methacrylate units are miscible with PS (4500 g/mol).

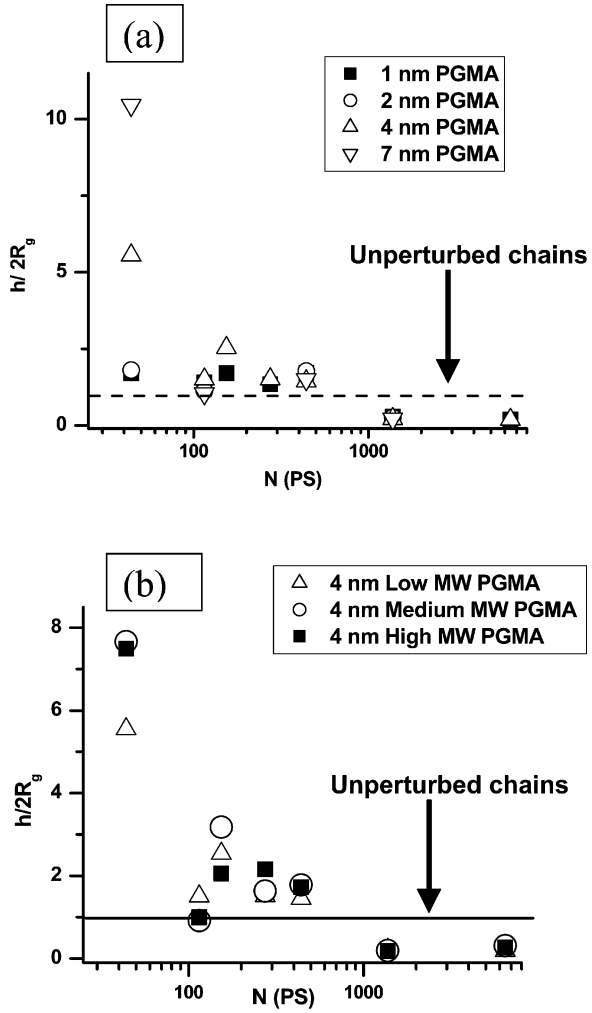

Figure 7. Grafted layer height (h) reduced to $2R_g$ vs degree of polymerization (N) of polystyrene layers grafted to (a) 1, 2, 4, and 7 nm PGMA (24 000 g/mol) layers and to (b) 4 nm PGMA layers of different molecular weights 24 000, 84 000, and 140 000 g/mol.

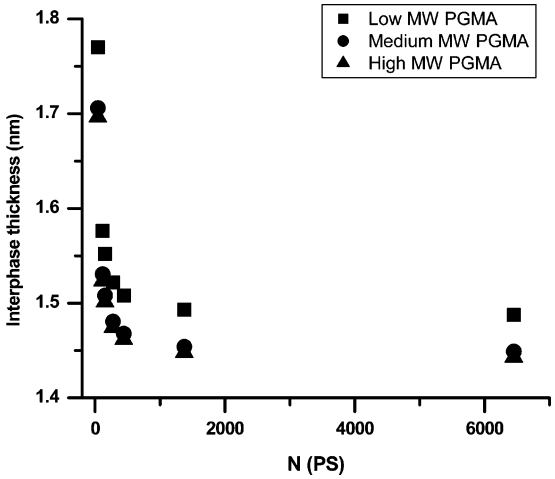

Figure 8. PS/PGMA interphase thickness vs degree of polymerization of PS, calculated for different molecular weights of PGMA using eq 9.

It has been reported that the train fraction for relatively high molecular weight polymers adsorbed on the surface is about 0.15−0.25, and on average 3−4 monomeric units are involved in the each train section.[37] Consequently, the average loop/tail size in the adsorbed

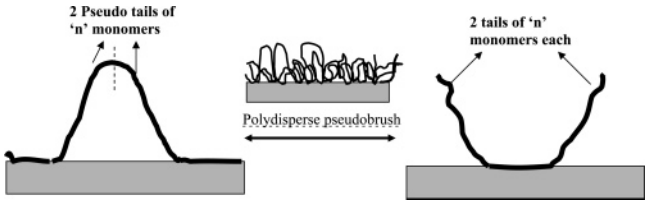

Figure 9. Pseudotail/tail conformations of PGMA in the adsorbed layer.

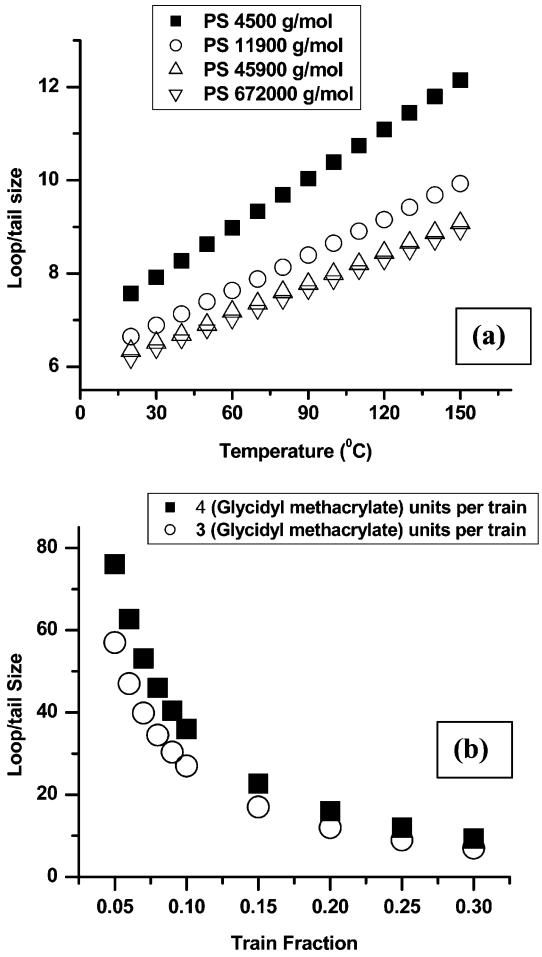

Figure 10. (a) Degree of polymerization of PGMA tails/loops vs temperature at which ΔG of PS/PGMA is equal to zero. (b) Loop/tail size vs train fraction.

PGMA layer may be estimated by a simple relationship:

$$\text{size} = \frac{N(1-p)}{Np/n} = \frac{(1-p)n}{p} \qquad (11)$$

where N is the degree of polymerization of the adsorbed polymer, p is the fraction of the monomeric units in the trains, and n is the number of the monomeric units involved in the one train section of the adsorbed macromolecule. Figure 10b shows the loop/tail size for the different train fractions. An average loop/tail size of 23 units corresponding to a train fraction of 0.15 and 4 monomeric units per train would be the upper bound value, while loop/tail size of 9 units corresponding to a train fraction of 0.25 and 3 monomeric units per train would be the lower bound. It is evident from Figure 10a that only PS (4500 g/mol) would be in the perimeter of our miscibility estimations for train fractions above 0.2. However, the size of the PGMA loops/tails in fact increases (or the fraction of the adsorbed chain in the trains decreases) as the thickness of the anchoring layer increases.[38] It therefore becomes also necessary to explain the increase in the amount of PS (M_n = 4500 g/mol) grafted with the increase in the thickness of the adsorbed PGMA layers in terms of the interdiffusion, since the longer loops while immiscible may form extremely extended PS/PGMA interphase. Interphase thickness (calculated using eq 9) for different molecular weights of PS and for various PGMA pseudobrush loops/tails sizes are represented in Figure 11. For PGMA loops of size less than 18 monomeric units, an extended interphase with PS (4500 g/mol) is predicted. Indeed, the loop size of 18 monomeric units lies close to the upper bound values of the loop/tail sizes. For higher molecular weight PS (employed in the present work) the calculated onset of the formation of the extensive interface is closer to the lower bound values of the loop/tail sizes. The miscibility/interface estimations indicated that PS (4500 g/mol) has significant tendency to penetrate into the adsorbed PGMA layer, while for the higher molecular weight polymers this tendency is not pronounced. The miscibility of the low molecular weight polymer with the PGMA loops and/or formation of the extended interphase could result in the "Echelon grafting" (grafting at much deeper levels of the anchoring layer of PS (4500 g/mol)). The "Echelon grafting" of low molecular weight PS caused the high surface coverage (Figure 4) and grafting density as the thickness of PGMA was increased. The obtained grafted layers cannot fall in the classical definition of a "polymer brush" anymore due to formation of semiinterpenetrating network-like structures. The random nature of diffusion for the low molecular weight PS permits formation of complex structures with fractal characteristics.[33] The fractal nature of the diffusion front in the case of thicker PGMA interlayer results in the rough structure of the low molecular weight grafted layer.

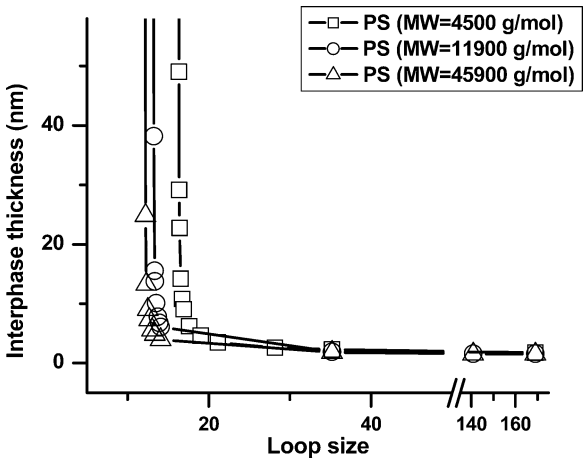

Figure 11. PS/PGMA interphase thickness calculated for different loop/tail size of PGMA using eq 9.

Before making conclusions from the presented work, it is necessary to mention a factor that may additionally affect the grafting under consideration. During the attachment of an end-functionalized polymer to the macromolecular anchoring layer at elevated temperature, besides reaction between end groups of PS and epoxy functionalities of PGMA, self-cross-linking of the PGMA film may occur.[21] The cross-linking side reactions may furthermore reduce the anchoring possibilities for the longer chains, without significant effect on the attachment of the shorter macromolecules.

Conclusions

The grafting of end-functionalized polymers employing the macromolecular anchoring layer approach was further investigated considering the effect of the molecular weight and thickness of the PGMA layer. The obtained experimental data indicate that, when the higher molecular weight PS chains are considered, neither the thickness nor the molecular weight of the PGMA layer has any significant influence on the grafting of the end-functionalized PS to the macromolecular anchoring layer. Conversely, the lower molecular weight PS sample does not follow the trend, since significantly higher amounts of the polymer can be grafted to the thicker anchoring layers. The high grafting in this case may be a result of formation of an extremely extended interphase between loops of the adsorbed PGMA and the low molecular weight PS.

In general, it was shown that until a certain level of miscibility/compatibility between a polymer being grafted and the anchoring macromolecules (attached to a substrate) is reached, the effect of the layer thickness and molecular weight is not pronounced significantly. However, in the case of such miscibility/compatibility the effect may become dramatic. We believe that the reported work presents the borders of the developed macromolecular anchoring layer technique in terms of miscibility and interpenetration. Specifically, if end-functionalized polymer is miscible/compatible with the anchoring layer, the thickness and molecular weight of the anchoring layer must be seriously taken into account to avoid (or reach) the extensive interpenetration at the boundary.

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