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Penetration of Polymer Brushes by Chemical Nonidentical Free Polymers

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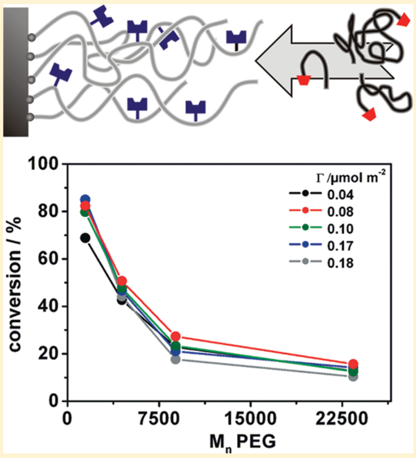
S *Supporting Information*

ABSTRACT: We report on the reaction of surface-attached polymer brushes with polymer molecules, which are present in a contacting solution. More specifically, we synthesize copolymer brushes containing *N*-hydroxysuccinimide active ester groups and study their reaction with poly(ethylene glycol) molecules, which carry an amino group at one end. Qualitatively, highly "pegylated" surfaces are obtained with an equivalent thickness of the PEG layers of up to 200 nm. Yield and kinetics of the grafting reaction are studied as a function of size and concentration of the incoming molecules, brush graft density, and brush molecular weight. It is observed that the completion of the grafting reaction is surprisingly fast, the molecular weight of the incoming molecules has a strong, while graft density and molecular weight of the brush have only a weak influence on the extent of functionalization. We develop a model for the grafting reaction, where due to limited penetration of the brush by the incoming chains the reaction occurs only at the outer periphery of the surface-attached layer. Reactive groups present in the inner parts of the brush do not take part in the attachment reaction. In the outer parts of the brush, however, partial penetration is possible so that the attachment reaction is fast and essentially only governed by the details of the shape of the segment density distribution and the size of the incoming chains.



I. INTRODUCTION

The interaction of a material with the surrounding medium is dominated by processes occurring at its surface. To tune these interactions, several methods have been developed in which polymer molecules are bound to the substrate surfaces by chemical bonds.[1−5] An interesting case, which has been intensely studied in the past 20 or so years, is where the polymer molecules are bound to the surfaces with such a high graft density that the polymer chains overlap and accordingly stretch away from the surface when they are in contact with a solvent.[6] Such systems are commonly referred to as "polymer brushes". They exhibit rather unusual physical properties, as the stretching of the chain reduces the conformational entropy of the chains and renders the penetration by large molecules or particles from the contacting solution highly unfavorable.[7]

In many cases, especially when biological applications are concerned, it is desired to incorporate specific functionalities into the brush layer such as cell recognition moieties or specific charged groups, to name just two examples.[8,9] It is usually not easily possible to introduce the desired functionalities into the monomer and then generate the brush as this would require large amounts of the frequently expensive monomer in order to obtain sufficiently high molecular weight chains. As an alternative, first brushes with reactive groups are prepared, which are then transformed by chemical reactions to yield the final, functionalized layer. It is therefore important to know how and to what extent polymer brushes can be transformed in such functionalization reactions.[10−14] It has been demonstrated that, as far as low molecular weight molecules are concerned, quantitative conversion can be obtained; however, for high molecular weight reactants the yield of the surface reaction was shown to be no longer quantitative.[15] This is not surprising as it is an important feature of brushes to exclude polymers and particles due to the entropy caused by chain stretching which cannot be compensated by the entropy of mixing (Figure 1).[16,17] This concerns both free and surface bound polymer molecules, as the coiled free polymers have to stretch for penetration and the brush has to respond to the increasing crowding, or in other words increasing segment−segment interactions, through stretching as well.

The penetration of brushes by free polymers and by contacting other brushes has been the subject of extensive theoretical studies and simulations for more than two decades.[7,18−31] For example, the penetration of block copolymer brushes by free polymers was studied experimentally by using nuclear reaction analysis and neutron reflectivity.[32,33]

A case where the penetration of brushes by free polymer chains is of particular importance is that where polymer chains are covalently attached to a surface through the reaction of functional groups on the polymer chains with appropriate

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Figure 1. Schematic depiction of the penetration of polymer brushes by low (left) and high (right) molecular weight molecules.

reactive sites at the surface of the substrate ("grafting to" reactions). This situation represents essentially a combination of penetration of the chains into the already grafted layer and attachment of the penetrating chains to the surface.[34−37] As the surface reaction is usually sufficiently fast, the rate of the grafting reaction is completely dominated by the rate of the penetration of the free molecules into the brush. Once the surface attached polymer chains start to overlap, they build up a strong barrier against further attachment of chains. Thus, the further grafting reaction is very strongly slowed down and takes place only on a logarithmic time scale.[35]

In general, the penetration depth increases with increasing concentration and decreases with increasing degree of polymerization of the free polymer P and reduced graft density Σ. The latter parameter is a measure for the degree of overlapping of the grafted chains and is calculated according to

$$\Sigma = \frac{\pi {R_g}^2}{D^2} \qquad (1)$$

where R_g is the radius of gyration and D the distance between two graft points.[38]

The dependence of the extent of penetration on the molecular weight and on the graft density of the attached chains Γ was experimentally confirmed, but also significant deviations from the predicted behavior have been reported.[39] The latter results indicate that the penetration of the brush by free chains might be far more pronounced than expected.

The present paper reports about experiments on the penetration of a polymer brush by chemical nonidentical free polymer chains. The brush contains reactive groups which can react with corresponding functional end groups of the incoming polymer. In our system the reactive groups are distributed throughout the brush layer so that even partial penetration of the brush leads to grafting reactions. However, once penetration of the brush by a free chain occurs, it becomes irreversibly bound, so that the location of the incoming polymer in respect to the brush becomes "frozen in". More in detail, poly(ethylene glycol) (PEG) chains with a terminal amine group are brought into contact with to a poly(methyl methacrylate) copolymer brush containing active ester (= succinimide ester) groups. The yield of the graft reaction is monitored through measuring the dry thickness of the brush as a function of the reaction conditions with ellipsometry. The influence of different parameters, such as graft density, molecular weight of the brush and the free polymer, and the concentration of the amine solution, onto the yield of the grafting reaction is elucidated.

II. EXPERIMENTAL SECTION

A. Materials. All chemicals were obtained from Sigma-Aldrich and used without further purification unless otherwise noted. Toluene and triethylamine were dried with sodium benzophenone and CaH_2, respectively. Methyl methacrylate was filtered over aluminum oxide 90 (Carl Roth) and distilled under exclusion of oxygen. Silicon substrates (polished on both sides) were purchased from Si-Mat and used without further cleaning.

B. Synthesis of the Active Ester Monomer. The succinimide ester monomer was synthesized from methacryloyl chloride via an amide formation with β-alanine and subsequent formation of the active ester with *N*-hydroxysuccinimide. Details of the synthesis have been reported elsewhere.[15]

C. Synthesis of the Azo-Initiator 4,4′-Azobis(4-cyanopentanoic acid−(3′-chlorodimethylsilyl)propyl ester) (ADS). The initiator was obtained by esterification of the acid chloride of 4,4′-azobis(4-cyanopentanoic acid) with allyl alcohol followed by hydrosilylation with dimethylchlorosilane as reported elsewhere.[40−42]

D. Immobilization of ADS on SiO_x Substrates. The SiO_x substrates were dried in vacuo and the immobilization of ADS (2 mL from a 50 mM stock solution in toluene) was performed under dry conditions in a Schlenk tube in toluene (60 mL) with NEt_3 (1 mL). After 16 h the substrates were cleaned with methanol and toluene and dried with nitrogen.

E. Polymerizations. Initiator-modified substrates were placed in a Schlenk tube and covered with the desired mixture of MMA and succinimide monomer in DMF. The solution was degassed 5 times by applying vacuum and filling back with nitrogen. The solutions were heated to 60 °C for 2−16 h depending on the desired graft density. The polymer which is generated in solution was precipitated in methanol, dried in vacuo, and characterized by NMR and GPC. The substrates with the polymer brushes were extracted with DMF (five times followed by drying with N_2).

F. Aminolysis of the Active Ester Brushes. The PMMA brushes containing active ester groups were placed in a sample bottle with the desired amino-PEG (33 mg), NEt_3 (50 μL), and DMF (1 mL) and heated to 40 °C for 16 h. The substrates were extracted with DMF as described before and dried with nitrogen.

G. FT-IR Spectroscopy. FT-IR spectra were recorded on a Varian BioRad Excalibur FTS 3000 in a spectral range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} in transmission mode. Therefore, the polymer brushes were synthesized on two side polished silicon wafers.

III. RESULTS

A. General Description of the System. In the present paper we focus on the behavior of reactive polymer brushes in contact with incoming polymers of different molecular weights. To this we synthesized copolymer brushes, which consist mainly of MMA and contain a small amount of *N*-hydroxysuccinimide ester groups (3−11%) as depicted schematically in Figure 2a. The brushes were synthesized by free radical surface-initiated polymerization ("grafting from") initiated by the thermal decomposition of a surface-attached initiator monolayer generated from 4,4′-azobis(4-cyanopentanoic acid−(3′-chlorodimethylsilyl)-propyl ester) (ADS) at 60 °C (Figure 2b).

The graft density and the molecular weight of the brushes were varied by adjusting the reaction time and the monomer concentration, respectively. The graft density and accordingly the dry thickness of the synthesized brushes increase with polymerization time (Figure 3a). The graft density Γ was calculated from the measured thickness and the molecular weight of the free polymer according to

$$\Gamma = \frac{d\rho}{M_n} \tag{2}$$

where d is the dry thickness, ρ the bulk density, and M_n the molecular weight of the brush. Details on the synthesized brushes can be found in Table 1 where also the reduced graft density values are listed. The obtained graft densities demonstrate that all samples are strongly in the brush regime.

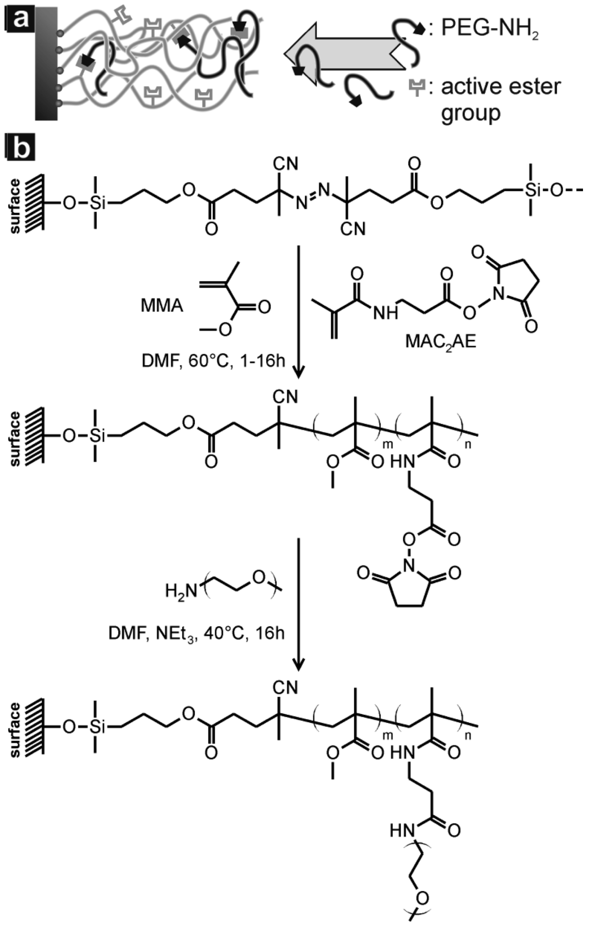

Figure 2. (a) Schematic depiction of active ester copolymer brushes in contact with end-functionalized amino-PEG. (b) Synthesis of reactive brushes from a monolayer of an azo-initiator (ADS) using a mixture of MMA and an active ester bearing methacrylate monomer. Monoamino-functionalized PEG of different molecular weights penetrate into the brushes swollen in DMF swollen brushes and react with the active ester groups in a subsequent amidation reaction.

Figure 3b shows FT-IR spectra (normalized to the ester band of MMA) of a series of PEG molecules grafted to selected active ester copolymer brushes. With increasing molecular weight of the PEG the signal of the C−O−C vibration band at 1107 cm^{-1} increases, indicating that a substantial amount of the brush consists of PEG after the grafting reaction.

The rationale behind the introduction of MMA as a base polymer is twofold: on the one side, MMA has a rather low transfer constant and thus allows to generate higher molecular weight polymer chains and thus thicker films. On the other side, dilution of the active groups by inert repeat units avoids strong crowding of the attached PEG chains. In most experiments the active ester concentration was chosen to 6%. The hydrodynamic radius of a PEG with a molecular weight of M_n = 25 000 (which is roughly the same as the molecular weight of the largest PEG used in the experiments described here) is R_H = 5.5 nm.[43,44]

Table 1. Molecular Characteristics of the Generated Brushes

sample no.	active ester content (%)	thickness/ nm	Γ/ μmol m^{-2}	M_n	Σ
1	6.2	13.3	0.04	370 000	2.8
2	6.2	22.8	0.08	340 000	5.0
3	6.2	30.6	0.10	380 000	6.8
4	6.2	46.5	0.17	320 000	9.7
5	6.2	57.3	0.18	380 000	12.3
6	6.2	26.0	0.17	180 000[a]	5.4
7	6.2	46.3	0.18	300 000	9.6
8	6.2	60.0	0.16	460 000	13.2
9	6.2	82.0	0.16	610 000	17.5
10	3.5	36.1	0.07	620 000	8.1
11	10.5	42.1	0.09	560 000[a]	8.6

[a] M_n could not be measured since there was not enough material formed in solution. Therefore, a mean value of Γ was taken from comparable experiments.

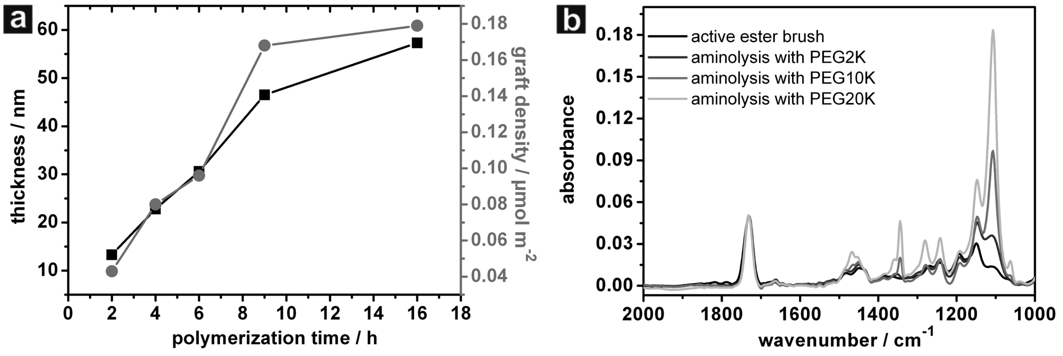

Figure 3. (a) Evolution of the brush thickness and graft density as a function of polymerization time. (b) FT-IR spectra of the active ester brush (black line) and the same brush after aminolysis with PEGs of different molecular weights.

Table 2. Molecular Weights of the Employed PEG

PEG name	750	2000	5000	10 000	20 000
M_n[a] (g/mol)	760	1450	4450	8850	23400
dispersity	1.05	1.06	1.17	1.29	1.22

[a] M_n was determined with SEC against PEG standards.

Therefore, when the size of the molecule is compared with the average distance of the active ester units along the chain (4.2 nm), it can be concluded that only for the largest PEG molecule and only at high conversion (above 40%) a slight "bottle brush brush" effect is expected.

In a standard experiment the dry thickness of the brushes was measured with multiple angle ellipsometry; the molecular weight and composition of the polymer were determined by GPC and NMR from the polymer formed in solution. The active ester brushes were then reacted with monoamino-functionalized PEG of varying molecular weights. After extensive washing with DMF to remove nonbound polymers, the dry thicknesses of the graft brushes were measured again. The ratio of the thickness after grafting d_2 to the thickness before grafting d_1 can be expressed as follows:

$$\frac{d_2}{d_1} = \frac{M_{\mathrm{PEG}} f + M_{\mathrm{brush}}(1-f)}{M_{\mathrm{brush}}} \qquad (3)$$

where M_{PEG} is the average molecular weight of the repeat units of the brush after grafting, M_{brush} is the average molecular weight of the repeat units of the brush before grafting, and f is the degree of functionalization of the active ester groups.[15]

Equation 3 can be rearranged to give the degree of functionalization f (amount of reacted active ester groups):

$$f = \frac{\frac{d_2}{d_1} - 1}{\frac{M_{\mathrm{PEG}}}{M_{\mathrm{brush}}} - 1} \qquad (4)$$

Note that M_{brush} and M_{PEG} are calculated using the value for the active ester concentration in the polymer obtained by NMR and the molecular weight of the used amino-PEG determined by SEC, respectively (for details on the amino-PEG see Table 2). It should be noted that even small experimental errors in the determination of the active ester contents have a rather large impact on the calculated values for the degree of functionalization. The reason for this is that the active ester contents of the different polymers are determined by NMR, and the accuracy of the integration of small NMR signals is limited. Therefore, the obtained values for the degree of the functionalization f should not be taken absolute but rather as a guidance to compare similar experiments within a series. A value less sensitive to these systematic errors is the normalized amount of grafted PEG m_{norm} which is calculated directly from the measured thickness values according to

$$m_{\mathrm{norm}} = \frac{m_{\mathrm{PEG}}}{m_1} = \frac{m_2 - m_1}{m_1} = \frac{m_2 - \frac{d_1}{d_2} m_2}{\frac{d_1}{d_2} m_2} = \frac{1 - \frac{d_1}{d_2}}{\frac{d_1}{d_2}} = \frac{d_2 - d_1}{d_1} \qquad (5)$$

with $M_{\mathrm{PEG}} = M_2 - M_1$ and $M_1 = (d_{1/}d_2)M_2$ (assuming that the density of the polymer stays constant).[15] Here, m_{norm} describes how much PEG was grafted in relation to the initial brush mass or how the thickness increased due to PEG attachment in relation to the initial brush thickness.

B. Characterization of the Grafting Reaction. To obtain a better understanding of the PEG attachment process, first some parameters that influence the grafting reaction were evaluated. In Figure 4 the brush thickness is shown exemplarily as a function of the reaction time for two different PEG solutions having the same segment concentrations (0.75 mmol). In comparison to other reactions involving brush penetration, it should be noted that the reaction is very fast and is already finished after 5 s for low molecular weight PEG 2K and roughly after 4 min for PEG 20K.

To exclude that the obtained results of the grafting process are largely influenced by the reaction kinetics, the reaction times of all aminolysis reactions described in the following were set to 16 h.

The influence of the concentration of the free polymer on the degree of functionalization was investigated at the example of the aminolysis reaction with PEG 5K (Figure 4b). The degree of functionalization increases with the concentration of the free polymer and seems to reach a plateau at about $c \sim 2.5$ mmol/mL. However, as the highest molecular weight PEGs are not soluble at such high concentrations, a compromise between extent of reaction and solubility of the polymer must be made. Accordingly, all following reactions are conducted at the same segment concentration of $c = 0.75$ mmol/mL.

C. Influence of the Molecular Weight of the Free Polymer. The influence of the molecular weight of the free polymer (PEG-NH_2) on the grafting reaction is shown exemplary for one brush in Figure 5. The PEG content in the brush (calculated from $(d_2 - d_1)/d_2$) after the grafting reaction is plotted as a function of the molecular weight of the PEG in Figure 5a. Qualitatively, it increases with the molecular weight in agreement with the FT-IR data shown in Figure 3b.

From these measured values the degree of functionalization f was calculated according to eq 4 and plotted as a function of the molecular weight of the free polymer (Figure 5a). The functionalization decreases from 95% for PEG 750 to 16% for PEG 20K, which indicates a strong influence of the molecular weight.

It can be expected that an important parameter for the penetration of brushes is the radius of gyration of the polymers, which scales in the investigated molecular weight region according to literature values with $R_g \sim M^{0.571}$.[45] From the linear dependence in Figure 5b it can be concluded that indeed the size of the incoming polymer molecules seems to be the figure of merit because for f we find an inverse proportionality to R_g:

$$f = k_1 \frac{1}{M^{0.571}} \qquad (6)$$

Another way to express the situation would be to describe the relation between the grafted mass and the molecular weight of the incoming chains. As shown in eq 5, the grafted mass normalized to the initial mass of the brush m_{norm} is directly accessible from the measured changes in the thickness, if we neglect small variations in the density of the polymer due to the grafting reaction.[15] In addition, the grafted mass $(m_2 - m_1)$ should be a product of the degree of functionalization and the molecular weight of the grafted chain which gives the following dependency:

$$\frac{d_2 - d_1}{d_1} = \frac{m_2 - m_1}{m_1} = \frac{k_2 f M}{m_1} \qquad (7)$$

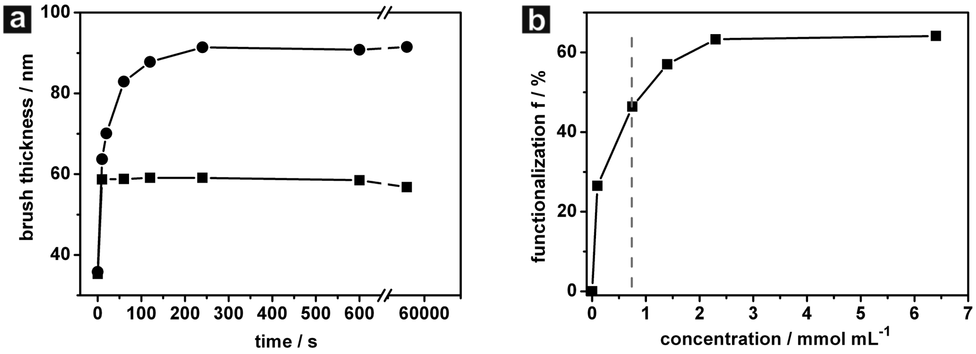

Figure 4. Brush dry thickness as a function of reaction time for the aminolysis of the active ester groups in the brush with PEG 2K (■) and 20K (●) (a). Functionalization as a function of the concentration of the PEG solution for PEG 5K. The standard concentration of all experiments was 0.75 mmol/mL as indicated by the gray dashed line (b).

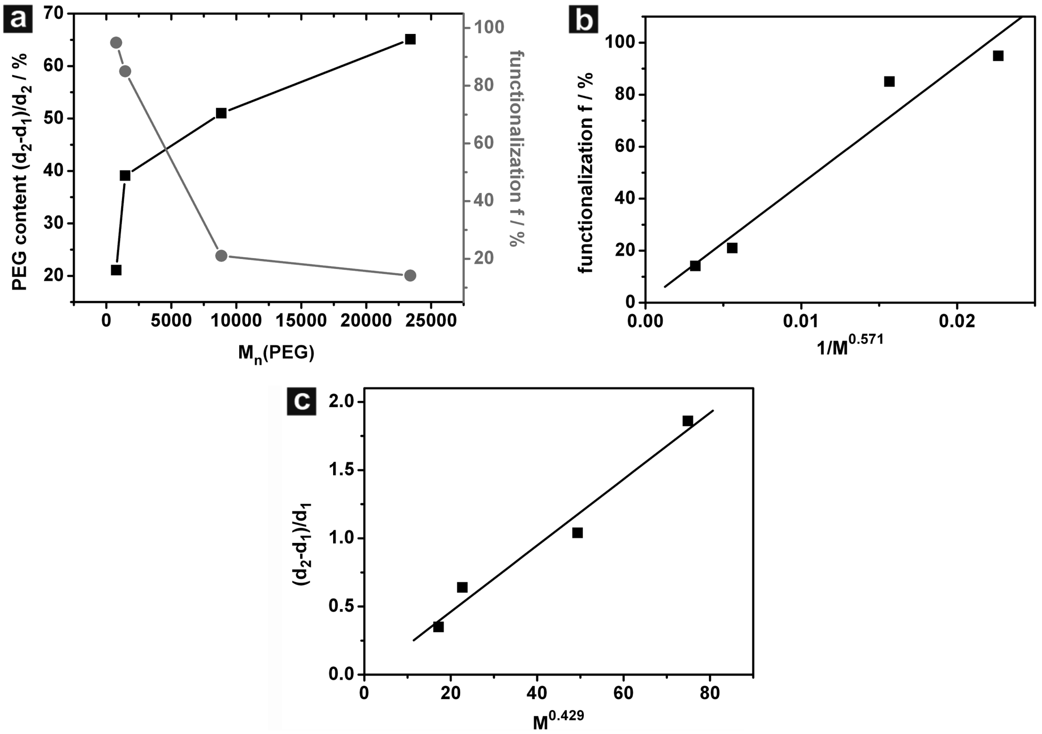

Figure 5. (a) PEG content (■) and degree of functionalization (●) as a function of the molecular weight of the free polymer for brush 4. (b) Functionalization as a function of $M^{-0.571}$ fitted with a linear fit through zero. (c) Amount of grafted PEG normalized to the brush thickness before grafting as a function of $M^{0.429}$.

Combining eqs 6 and 7 leads to

$$\frac{d_2 - d_1}{d_1} = k_3 M^{0.429} \qquad (8)$$

with $k_3 = k_2 k_1 {m_1}^{-1}$.

In Figure 5c $(d_2 - d_1)/d_1$ is plotted as a function of $M^{0.429}$. Although this is in principle only a different way to express the same data as before, it is still instructive as it shows that with increasing molecular weight of the incoming chains the PEG layer thickness increases slowly, with slightly less than a square root dependence, in agreement with the predictions of eq 8.

In another set of experiments we studied the aminolysis of an active ester brush, which had been already functionalized with PEG 20K, in a second reaction with PEG 10K and subsequently in a third with PEG 2K (Table 3). It should be noted that the conversion of the active ester groups is by far not quantitative, and still a large number of groups are available in the brush, which could potentially react. However, despite the large number of unreacted groups present, no increase in the dry thickness is observed for reaction with either molecular weight. This result indicates that even the small PEG 2K cannot penetrate the functionalized brush and reach the remaining active ester groups.

D. Variation of the Graft Density and the Molecular Weight of the Brush. The graft density Γ of the brushes was varied through adjustment of the polymerization time, so that a series of polymer layers with reduced graft densities from Σ = 2.8 up to Σ = 12.3 were obtained (Table 1). The brushes were cut into four pieces in each case, and the different amino-PEGs were grafted to the brushes. The resulting data for the PEG content show practically a linear relation of the grafted amount with the graft density (Figure 6a), but no influence of the graft density onto the functionalization (Figure 6c).

In a next set of experiments the influence of the molecular weight of the brushes on the grafting reaction was studied for two different molecular weights of incoming chains. To this the monomer concentration was varied during the surface-initiated polymerization, so that brushes were obtained with molecular weights ranging from 180 000 to 610 000. The graft density was the same for all polymers in this series. The grafted amount of PEG and the degree of functionalization are plotted as a function of the molecular weight of the surface-attached polymers (Figure 6b,d).

The overall picture is very similar to the results of the graft density series. While the grafted amount increases linearly with the molecular weight of the incoming chains (Figure 6b), the degree of functionalization of the active ester groups is hardly affected at all, and though the films vary quite strongly in the thickness, the percentage of converted active groups remains constant.

Table 3. Thickness of an Active Ester Brush for Subsequent Aminolysis Reactions

reaction step	M_n of amino-PEG	d/nm
0		27.0
1	20K	57.7
2	10K	58.8
3	2K	58.9

E. Dilution of Reactive Groups in the Brush. In a last set of experiments the amount of active ester groups was reduced systematically from 10.5% to 6.2% to 3.5%. The molecular weights of the three different series of brushes are not exactly the same as the extent of transfer during the generation of the different polymers depends on the monomer composition. However, we have shown above that variations in the molecular weight of the brush have no strong influence on the grafting reaction. The brushes were reacted with amino-PEG of varying molecular weights. In Figure 7 the normalized grafted mass of PEG is plotted as a function of the active ester contents. The amount of PEG in the brushes decreases upon dilution of the active ester groups for all molecular weights of the PEGs.

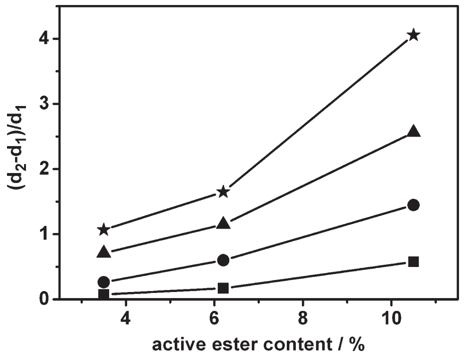

Figure 7. Relative amount of PEG in the brushes after aminolysis as a function of the active ester content in the brushes for polymers with different molecular weights: ■, PEG 750; ●, PEG 2K; ▲, PEG 10K; ★, PEG 20K.

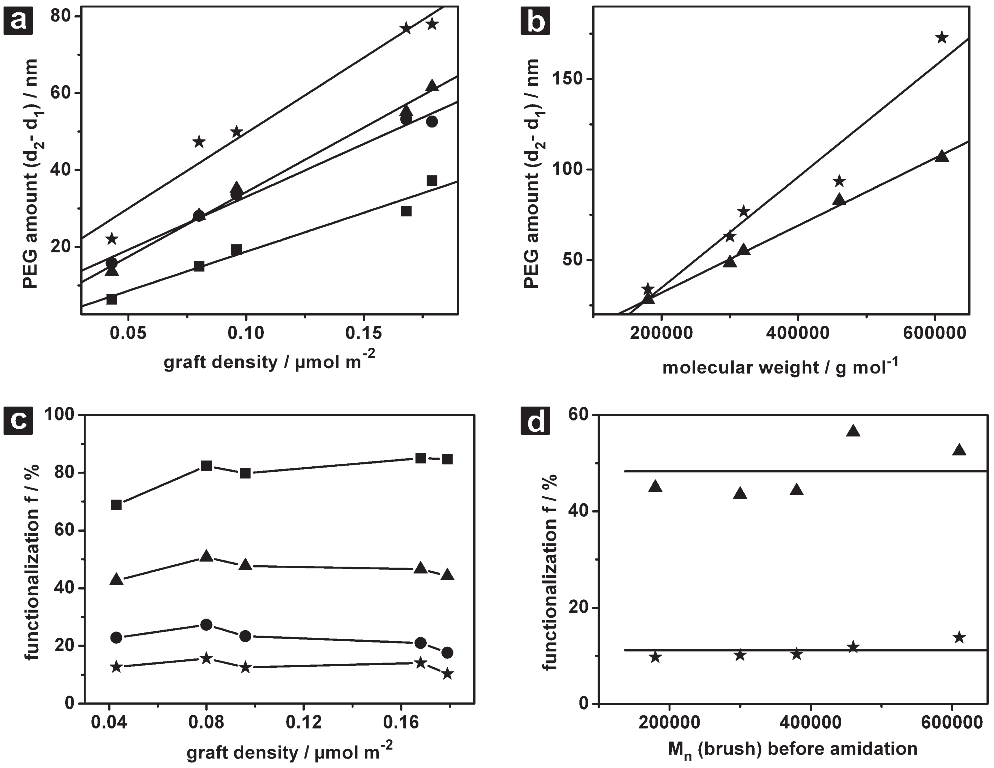

Figure 6. (a) PEG amount in the brushes after reaction with different molecular weight PEG molecules (■, PEG 2K; ▲, PEG 5K; ●, PEG 10K; ★, PEG 20K) as a function of the graft density and (b) the molecular weight of the brushes. (c) Plot of the degree of functionalization *f* as a function of the graft density and (d) molecular weight of the brushes.

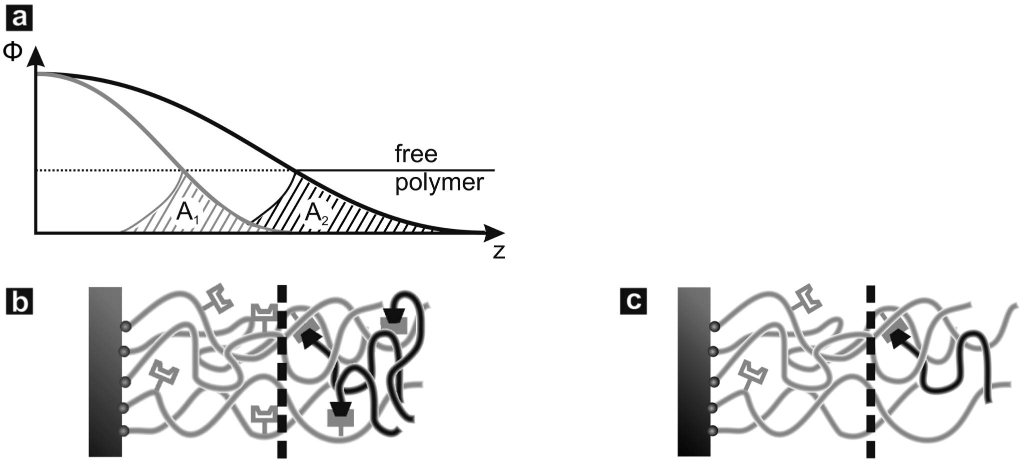

Figure 8. (a) Artist's impression of the segment density profile for two different molecular weight brushes in contact with free polymer, where the hatched region is the area of penetration. (b) Schematic depiction of the grafting situation in our experiments with high degree of functionalization at the periphery of the brush and (c) the same situation with lower active ester concentration.

IV. DISCUSSION

A model that sets out to explain the binding behavior of polymers into the surface-attached brushes has to be consistent with the following main observations:

Under appropriate conditions large amounts of PEG can be bound, e.g., for PEG 20K the total PEG content of the pegylated brush is 80% (Figure 7, ★) and for PEG 750 a degree of functionalization of 95% can be reached (Figure 5a), so that the incoming material increases the thickness (i.e., the mass) of the film by several hundred percent.

The extent of binding is a strong function of the molecular weight of the free chains (Figure 5).

The graft density of the surface-attached chains has no significant influence on the degree of functionalization (Figure 6a); however, the number of bound chains increases linearly with the graft density.

The binding process of the polymer attachment is very fast; after few minutes the process is essentially complete and no significant difference can be observed, even when very long reaction times are chosen (Figure 4a).

The strong influence of the molecular weight of the free polymer on the extent of polymer immobilization is expected from standard brush theory and is in good agreement with previous results.[19,46] Small molecules can easily penetrate a polymer brush due to a high entropy of mixing and allow essentially quantitative functionalization. For the binding of large molecules, however, the energy gain from the entropy of mixing becomes small so that it cannot offset the energy cost of stretching both the free and surface attached chains. As the size of the incoming chains is the figure of merit, the functionalization decreases proportional to the radius of gyration of the PEG chains as depicted in Figure 5b. We have used here the known scaling relation between the radius of gyration and the molecular weight of the PEG chains ($R_g \sim M^{0.571}$). If the amount of grafted PEG is viewed (Figure 5c), this mass is a product of the degree of functionalization and the molecular weight of the grafted chain (eq 7), and thus the amount of PEG in the brush increases proportional to $M^{0.429}$.

While this behavior seems to be rather straightforward, the dependence of the degree of functionalization on the graft density of the brush is at first view much more puzzling.

Intuitively, as the graft density determines the stretching of the surface-attached chains, one would expect the graft density of the brush to have a strong impact on penetration and thus binding of the incoming chains. This is obviously not the case.

According to the standard model of brushes, penetration will only occur at those locations that are below a certain critical segment density. Thus, the extent of functionalization is expected to be a strong function of the segment density profile of the brush. However, it should be noted that the segment density profile depends not only on the graft density of the chains but also on their polydispersity. The brushes studied here have been generated by free radical polymerization and are polydisperse ($M_n/M_w \sim 2.7$; measured for free chains isolated after polymerization), so that the segment density profile can be expected to have a long tail.[47]

The influence of polydispersity on the segment density profile was addressed by several groups.[48−50] Terzis et al. modeled brushes having polydispersities M_w/M_n ranging from 1 to 5 in contact with free chains using self-consistent mean-field theory. According to their results, the interfacial width, a measure of the region where grafted chains and free chains coexist in the brush, increases with the graft density of the brush in form of an exponential association function. In the range of graft densities experimentally accessible to us, however, this function is more or less linear. This implies that for a polydisperse brush the penetration zone grows directly proportional to the graft density. Thus, we should expect a linear growth of the number of accessible reactive groups with the graft density of the brush ($N^* \sim \Gamma$). However, as the total number of polymer brush segments is directly proportional to the graft density ($N \sim \Gamma$), the number of accessible segments in relation to the total number of segments is expected to be constant:

$$\frac{N^*}{N} = \frac{k_1 \Gamma}{k_2 \Gamma} = \text{const} \qquad (9)$$

This agrees well with the experimental results shown in Figure 6a where the degree of functionalization (and not the number of bound chains!) stays constant with increasing graft density.

Essentially the same argument holds true, if one simply increases the molecular weight of the brush. Theoretical work by Milner, Witten, and Cates on monodisperse brushes and also (implicitly) by Terzis et al. on polydisperse brushes[49,51] suggests that an increase in molecular weight leads to strong changes in the segment density and to an appropriate increase of the penetrable volume. The situation is schematically depicted in Figure 8a, where schematic segment density profiles for two polymers with different molecular weights are shown. The ratio of the areas A_1 and A_2 for the two different brushes (i.e., the volume where penetration of the brush is possible) in relation to the total integral under the curves (i.e., the total brush volume) is nearly the same. In accordance with these theoretical considerations the experimental data in Figure 6b show that the thickness/mass of the attached polymeric material increases directly proportional to the molecular weight of the brush, and thus no influence of the molecular weight of the brushes on the degree of functionalization can be observed.

The picture of a reaction at the periphery without significant penetration of the inner parts of the brush allows to explain the, at first view, rather unexpected fast kinetics of the reaction. As the reaction occurs only in the easily accessible outer perimeter of the brush, the attachment reaction can be expected to be very fast. Any polymer binding in the outer sections of the brush will increase the segment density there and accordingly sharpen the segment density profile further, which will in turn even more strongly prevent the binding of additional chains to inner parts of the brush, so that very rapidly a (quasi) asymptotic behavior is reached.

The model explains also the results of experiments, where a brush was first functionalized with high molecular weight PEG, e.g. PEG 20K, and later brought into contact with lower molecular weight polymers. In this case no further attachment of lower molecular weight PEG (e.g., PEG 2K) could be observed, despite the fact that still most of the active ester groups of the groups remain unreacted in the first reaction step. However, if we assume that most accessible units are consumed in the penetration zone, it seems consequent that no further reaction can occur.

A model which suggests that the functionalization in the penetrated region is nearly quantitative and in the inner parts of the brush nearly zero as (Figure 8b,c) helps to understand the results obtained for the dilution of active ester groups in the brush where the grafted PEG mass decreases with decreasing active ester concentration for all PEG samples studied (Figure 7). The model would predict that in such dilution experiments the accessible volume stays constant. Thus, the number of active ester groups contained in this volume decreases with decreasing active ester contents of the polymer. It should be noted that alternative models, which would explain the incomplete conversion of the active ester groups, e.g., with local steric reasons, could not explain this behavior. In such a case with decreasing active ester contents the steric situation should become more relaxed so that the bound mass should be only a weak function of the active ester contents.

V. SUMMARY AND CONCLUSIONS

The reaction of amino-functionalized poly(ethylene glycol) (PEG) with surface-attached polymer brushes carrying active ester groups allows to bind high quantities of PEG molecules to the brushes. Depending on the experimental conditions, the incoming PEG chains can contribute to as much as 80% of the total mass of the surface-attached film, and in some cases the active ester groups can be almost quantitatively reacted with the incoming polymer chains. Because of the attachment of the incoming, additional material the (dry) thickness of the surface-attached layer (and accordingly the mass of the film) can increase by several hundred percent, e.g., from roughly 50 to about 230 nm.

While the degree of functionalization decreases with the size of the free PEG molecules (and accordingly roughly with the square root of the molecular weight), the total amount of grafted PEG increases roughly with the square root of the molecular weight of the incoming chains.

We propose that the attachment behavior can be explained by a model in which penetration and subsequent attachment of free chains occurs only at the outer periphery of the brush, where the segment density is low. Only when the local segment density of the brush is below a certain critical value (which of course also depends on the concentration of the free chains in the contacting solution) partial penetration of the brush is possible. In the inner parts of the brush (i.e., those close to the surface) the segment density is high, so this volume cannot be penetrated by the free chains. Accordingly, the shape of the segment density distribution has an important influence on the attachment reaction. Thus, one of the key questions for the functionalization of a brush with high molecular weight molecules is how the different brush parameters, for example graft density, degree of swelling, polydispersity, and others, influence the shape of the segment density profile.

This model is able to explain the at first view surprisingly fast binding kinetics, in which the binding of the polymers to the brush is already complete after seconds or at the latest within a few minutes after beginning of the reaction. As the free chains can penetrate only the part of the brush where the segment mobility is high, the process is complete rather quickly and no further polymer attachment occurs.

The model can also explain why the degree of functionalization is largely independent from the graft density of the already attached chains while the number of attached chains increases with grafting density. As no penetration of the inner parts of the brush occurs anyways, increasing the graft density will not change the situation; it just has an influence on the size and shape of the penetrable zone.

The results of this work seem to allow us to make some predictions about other similar systems. If we assume that the extent of functionalization depends strongly on the shape of the segment density profile, then a more boxlike segment density profile will cause a smaller extent of penetration and functionalization. Thus, it might be concluded that all surface-attached layers which have a sharper segment density profile, such as narrow polydispersity brushes and surface attached polymer networks would allow only a very low degree of functionalization. Especially networks swell with a segment density profile, which is more delta function shaped and should accordingly be even more difficult to become functionalized with polymer molecules as polymer brushes. Experimental studies along these lines are currently performed in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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