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Neutron Reflectivity Study on the Postpolymerization Modification of Poly(2-hydroxyethyl methacrylate) Brushes

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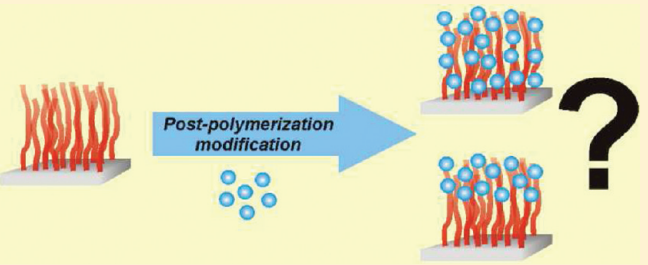
Supporting Information

ABSTRACT: Postpolymerization modification reactions are widely employed to prepare functional polymer brushes. Relatively little is known, however, about the distribution of functional groups in such postmodified brushes. Using neutron reflectometry and UV−vis spectroscopy as principal tools, this article investigates the *p*-nitrophenyl chloroformate (NPC)-mediated postpolymerization modification of poly(2-hydroxyethyl methacrylate) (PHEMA) brushes, prepared via surface-initiated atom transfer radical polymerization, with D-10 leucine and D-3 serine. The neutron reflectometry experiments indicate that the postpolymerization modification depends both on brush thickness and grafting density. Whereas for dense brushes, postpolymerization modification with D-10 leucine is limited to the top ∼200 Å of the brush, independently of the brush thickness, the extent of postmodification can be significantly enhanced by decreasing the grafting density of the brush or by using the more hydrophilic and sterically less demanding D-3 serine, which reflects the ability of this amino acid to more readily penetrate the brush. UV−vis experiments revealed that the NPC activation is also nonuniform, but brush thickness and grafting density dependent, which adds to brush thickness and density and the nature of the amino acid as another of a complex set of variables that determine the final distribution of functional groups in postmodified brushes.



INTRODUCTION

Polymer brushes are ultrathin, surface grafted polymer layers in which all polymer chains are tethered with one of their chain ends to a substrate.[1−5] At sufficiently high grafting densities, steric repulsions force the chains to stretch out, resulting in a densely packed arrangement of surface grafted polymer chains. The use of controlled/"living" surface-initiated radical polymerization techniques allows to precisely control the thickness, composition, and architecture of polymer brushes, which makes them very attractive coatings to tune the surface properties of a broad range of materials.

For many applications, polymer brushes are required that contain specific functional groups. Functionalized polymer brushes can be prepared either via direct surface-initiated polymerization of the appropriate side-chain functional monomer or via postpolymerization modification of a suitable, reactive polymer brush. Although the relatively high functional group tolerance of "living"/controlled radical polymerization techniques allows the direct surface-initiated polymerization of a wide variety of side-chain functional monomers, there is still a large number of complex side-chain functional monomers that cannot be directly polymerized. Postpolymerization modification is an attractive alternative to overcome these problems and to enable the preparation of polymer brushes with complex functional groups. In spite of the fact that postpolymerization modification is a well-established strategy to synthesize functional polymer brushes,[1] only very little is known about the distribution of the resulting functional groups throughout the polymer brush layer. Steric constraints during the postpolymerization modification reaction, however, may result in a nonhomogeneous distribution of functional groups and concentration gradients throughout the polymer brush, which, in turn, may influence the final properties of the polymer brush.

This article describes the results of a study that was aimed at investigating the influence of film thickness and grafting density on the distribution of functional groups in a polymer brush prepared via postpolymerization modification. To investigate the location and distribution of functional groups in the polymer brush films, neutron reflectometry was used. This technique has already been used to determine the structure of neutral and polyelectrolyte brushes,[6−9] to monitor the swelling behavior of weak polyelectrolyte or thermosensitive brushes,[10−13] or to study the chain-end distribution in polymer brushes.[14] The experiments discussed in this article were performed with poly(2-hydroxyethyl

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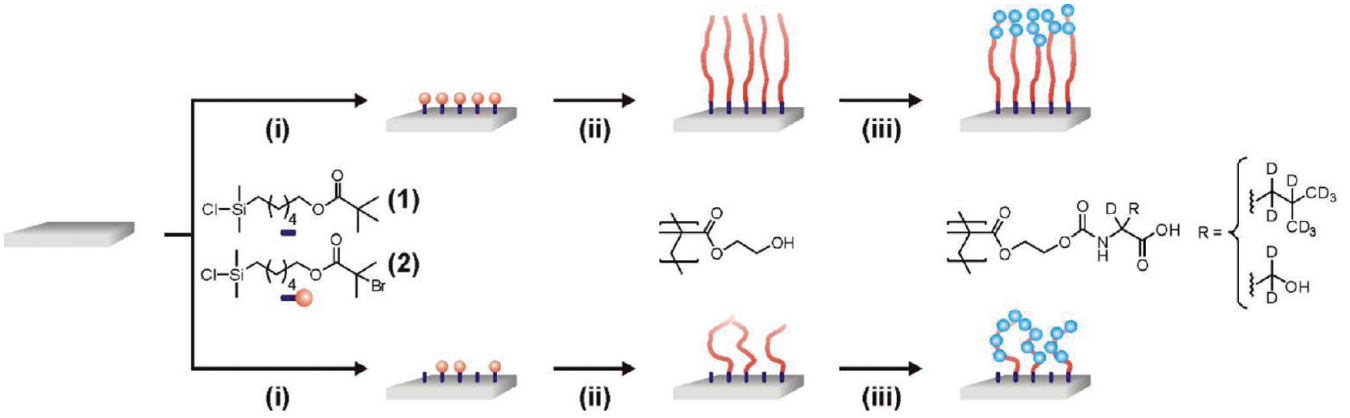
Scheme 1. Synthesis of PHEMA Brushes of Varying Grafting Density via SI-ATRP and Postpolymerization Modification with D-10 Leucine and D-3 Serine[a]



[a] (i) 10 mM solution of **2** (upper part) or 10 mM mixture of **1** and **2** (lower part) in toluene, overnight; (ii) H_2O/HEMA/CuCl/$CuBr_2$/2,2′-bipyridyl; (iii) NPC/Et_3N/THF, 1 h; amino acid/DMAP/DMF, 16 h followed by quenching with ethanolamine.

methacrylate) brushes, which were postmodified with deuterated leucine (D-10 leucine) and deuterated serine (D-3 serine) after activation of the side-chain hydroxyl groups with *p*-nitrophenyl chloroformate (NPC). The NPC activation strategy is commonly used for the postpolymerization modification of hydroxyl side-chain functional polymer brushes.[15−19] The distribution of the D-10 leucine and D-3 serine residues in the final polymer brush films was determined by neutron reflectivity, taking advantage of the neutron scattering contrast between hydrogen and deuterium.[20] The ability to understand and measure the distribution of functional groups in polymer brushes prepared via surface-initiated atom transfer radical polymerization is important not only as it may provide guidelines for the synthesis of homogeneous functional brushes but also since it may indicate opportunities to, via judicious choice of the reaction conditions, produce nonhomogeneous, but precisely controlled, polymer brushes. The latter may lead to polymer brushes with new and interesting properties.

EXPERIMENTAL SECTION

Materials. Deuterated amino acids (D-10 leucine and D-3 serine) were purchased from Cambridge Isotope Laboratories, Inc. All other chemicals were obtained from Aldrich and used as received unless otherwise stated. The polymerization inhibitor in 2-hydroxyethyl methacrylate (HEMA) was removed by passing the monomer through a column of activated basic aluminum oxide. Organic solvents were dried using a Pure Solv 400 solvent purification system. For neutron scattering experiments, rectangular silicon substrates with a thickness of 525 ± 25 μm and dimensions of 50 × 75 mm were used. The ATRP initiator, (6-(2-bromo-2-methyl)propionyloxy)hexylchlorosilane, was synthesized and immobilized onto the substrates as previously described.[21] The ATRP inactive, 6-((chloro(dimethyl)silyl)hexyl pivalate, was synthesized via the same method using pivalyol chloride instead of α-bromoisobutyryl bromide.

Methods. Neutron reflectometry experiments were performed at the Swiss Spallation Neutron Source (SINQ) at the Paul Scherrer Institute (Villigen, Switzerland) using the AMOR time-of-flight reflectometer (neutron wavelength range from 2 to 12 Å).[22,23] The reflectivity was recorded at three angles of incidence (0.3°, 0.9°, and 1.9°) in order to cover a wide scattering vector (q) range. The data were fitted with the MOTOFIT package,[24] using a five-layer model: bulk Si/SiO_2/PHEMA/postmodified PHEMA/air. The scattering length density (SLD) profiles were obtained by fitting the experimental reflectivity data. The scattering data were modeled assuming that the concentration of the deuterated groups is highest at the brush−air interface and that for a given amino acid this maximum concentration was the same for all samples. The thicknesses of the various polymer brushes were extracted from the fitted reflectivity data. The volume fraction of deuterated compound at a distance z from the surface $\phi(z)$ was determined from the scattering length density profile using

$$\phi(z) = [\rho(z) - \rho_{PHEMA}]/[\rho_D - \rho_{PHEMA}]$$

in which $\rho(z)$ is the SLD determined from the fit at the distance z of the surface, ρ_{PHEMA} is the experimental SLD of PHEMA (0.990×10^{-6} Å^{-2}), and ρ_D is the experimental SLD of the postmodified PHEMA at the brush−air interface, namely 1.700×10^{-6} Å^{-2} for the PHEMA postmodified with D-10 leucine and 1.7265×10^{-6} Å^{-2} for the PHEMA postmodified with D-3 serine (these values were used for all the fittings). The theoretical SLD values for PHEMA, D-10 leucine, and D-3 serine postmodified PHEMA were estimated to 1.10×10^{-6}, 2.320×10^{-6}, and 2.240×10^{-6} Å^{-2}, respectively, using the National Institute of Standards and Technology (NIST) SLD online calculator.[25] Initial polymer brush thickness were measured by AFM with a Veeco Multimode Nanoscope IIIa SPM controller in tapping mode using NSC14/no Al Mikromasch cantilevers, on patterned polymer brushes that were prepared as previously described.[26] UV−vis absorbance spectra were recorded using a Varian Cary 100 Bio UV−visible spectrophotometer at room temperature on polymer brushes coated on quartz substrates.

Procedures. Surface-initiated atom transfer radical polymerization (SI-ATRP) of 2-hydroxyethyl methacrylate (HEMA) was preformed as previously described,[27] using H_2O/HEMA/CuCl/$CuBr_2$/2,2′-bipyridyl in a 400/60/1/0.3/2.8 molar ratio. The grafting density of the PHEMA brushes was varied by modifying the silicon substrate with a mixture of the ATRP initiator (6-(2-bromo-2-methyl)propionyloxy)hexylchlorosilane) and an equivalent ATRP passive molecule (6-((chloro(dimethyl)-silyl)hexyl pivalate), as reported before.[28] Grafting densities are given as the volume percentage of the ATRP initiator modified organosilane in the mixture of chlorosilanes that was used to modify the silicon substrate. Throughout this article, PHEMA brushes grafted from surfaces that are modified only with the ATRP initiator are referred to as dense brushes.

Postpolymerization modification reactions were carried out following a procedure reported earlier by Tugulu et al.[18] First, the polymer brushes were incubated for a period of 1 h in an anhydrous THF solution

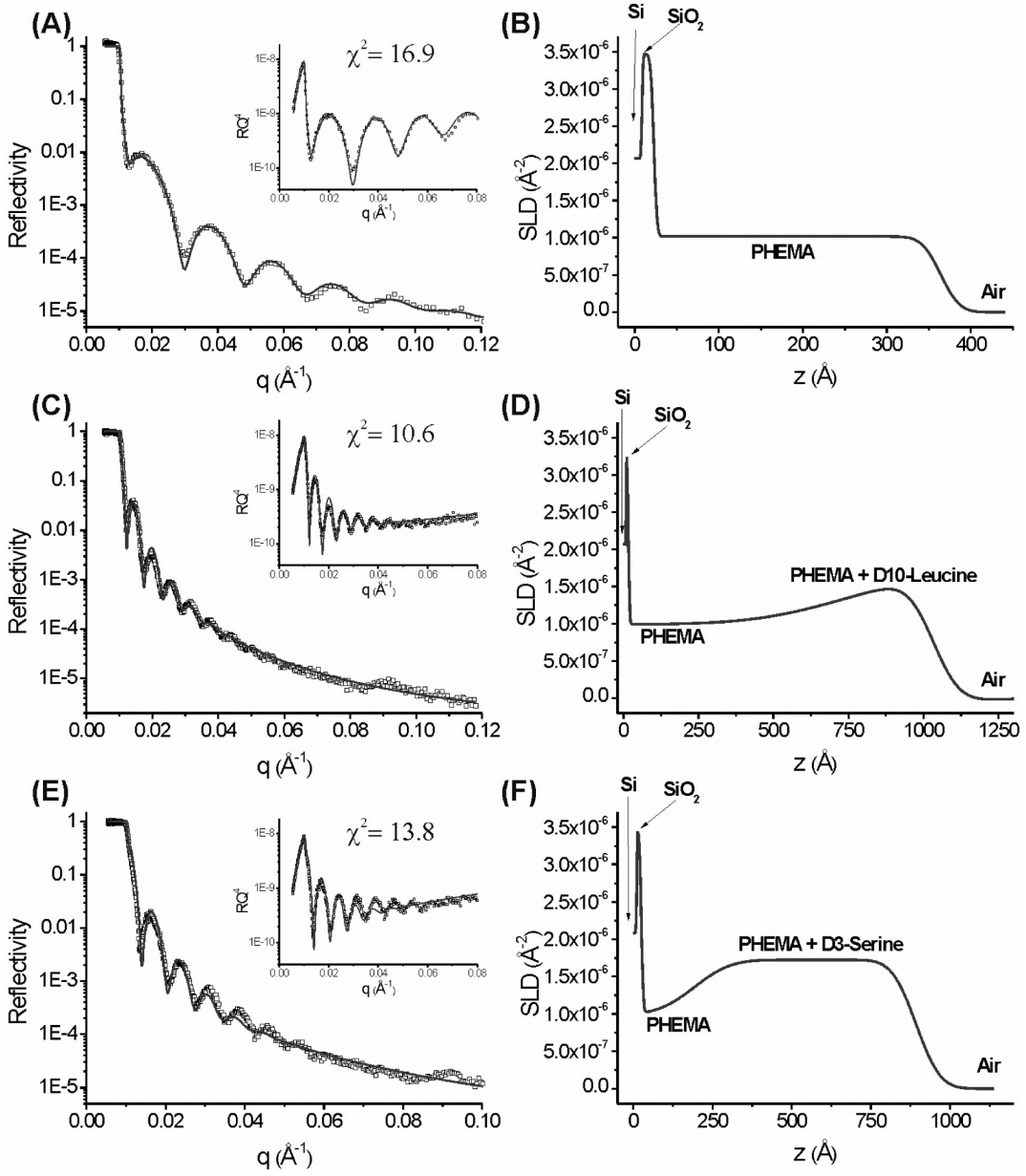


Figure 1. (A) Experimental reflectivity data (open squares) and the corresponding fits (solid lines) of (A) an unmodified 341 Å thick PHEMA brush, (C) a 1016 Å PHEMA brush after postpolymerization modification with D-10 leucine, and (E) a 867 Å thick PHEMA brush after postpolymerization modification with D-3 serine. Panels (B), (D), and (F) show the corresponding SLD profiles. The inserts in A, C, and E show the Rq4 versus *q* plots of the reflectivity profiles for a better appreciation of the fitting.

containing *p*-nitrophenyl chloroformate (35 mM) and triethylamine in a 1/1 molar ratio. After that, the substrates were left for a period of 16 h in an anhydrous DMF solution containing 1 mM of deuterated amino acid (D-10 leucine or D-3 serine) and 2.5 mM of 4-(dimethylamino)pyridine (DMAP). Any remaining carbonate groups in the polymer brush were quenched by exposure to a 0.5 M solution of ethanolamine in anhydrous DMF for 30 min, and the samples were subsequently thoroughly rinsed with ethanol and methanol and finally dried under nitrogen.

■ RESULTS AND DISCUSSION

The postpolymerization modification of the PHEMA brushes that is investigated in this study is illustrated in Scheme 1. To evaluate the effects of brush thickness and grafting density, a library of PHEMA brushes was prepared with thicknesses of up to ~880 Å and grafting densities, expressed as the volume percentage of the ATRP initiator in the mixture of chlorosilanes that was used to modify the substrates of 25, 50, 75, and 100%. Among the variety of strategies that is available to postmodify hydroxyl-containing polymer brushes,[1] this article uses the *p*-nitrophenyl chloroformate (NPC)-mediated functionalization with amines. While other and more efficient approaches may be available, this strategy was chosen as it is widely used to postmodify PHEMA and other hydroxyl-containing polymer brushes[15−19] and thus represents an interesting system to explore the feasibility of neutron reflectometry to probe the location and distribution of functional groups in the postmodified brushes.

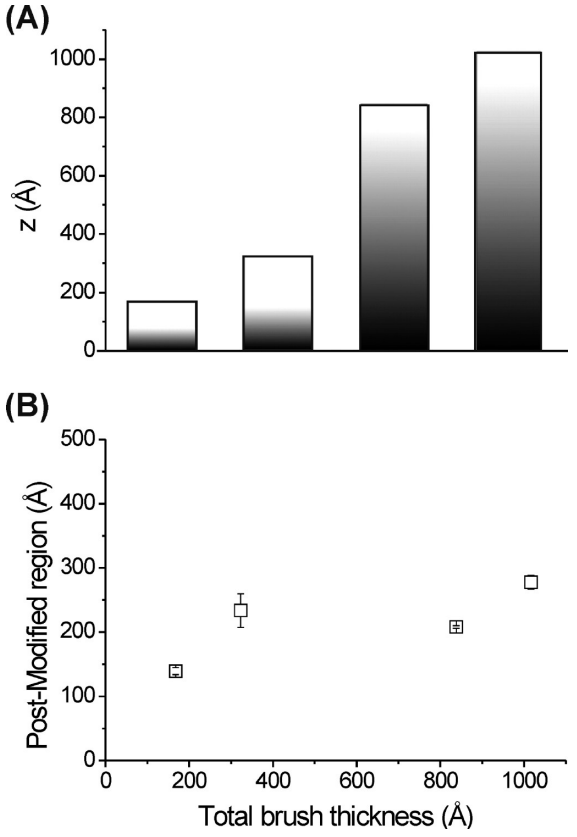


Figure 2. Influence of film thickness on the postpolymerization modification of dense poly(2-hydroxyethyl methacrylate) brushes with D-10 leucine. (A) Total thickness (bars) and thickness of the postmodified layer (top white area) for brushes of different thicknesses. (B) Thickness of the D-10 leucine postmodified region as a function of the total PHEMA brush thickness. The data in (B) represent the average of two independent neutron reflectometry experiments on different samples that were prepared under identical conditions. For some data points the error bars overlap with the data points and are invisible.

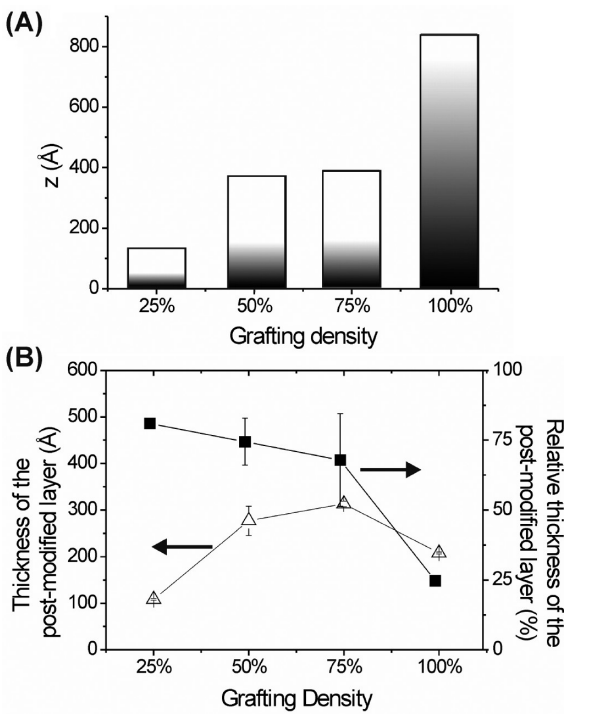


Figure 3. Influence of grafting density on the postpolymerization modification of poly(2-hydroxyethyl methacrylate) brushes with D-10 leucine. (A) Total thickness (bars) and thickness of the postmodified layer (top white area) for brushes of different grafting densities. (B) Absolute thickness (△, left axis) and relative thickness (■, right axis) of the postmodified layer for PHEMA brushes of different grafting densities. The data in (B) represent the average of two independent neutron reflectometry experiments on different samples that were prepared under identical conditions. For some data points the error bars overlap with the data points and are invisible.

Since the NPC-mediated postpolymerization modification may depend on the nature of the amine that is used, PHEMA brushes were modified both with a polar and uncharged amino acid (serine) as well as with an amino acid that bears a hydrophobic and bulky side chain (leucine).

The postmodified brushes were studied by neutron reflectometry. As a representative example, Figure 1 shows the experimental reflectivity profiles and the corresponding scattering length density profiles for a 341 Å unmodified PHEMA brush, a 1016 Å thick PHEMA brush after postmodification with D-10 leucine, and a 867 Å thick PHEMA brush after postpolymerization modification with D-3 serine. From the results obtained with the unmodified PHEMA brush, a SLD of 0.990×10^{-6} Å^{-2} was obtained, and this value was used for the subsequent fitting of the postmodified brushes. After an abrupt transition at the silicon oxide−brush interface, the scattering length density profile of the PHEMA brush remained constant until the last 42 Å, where there is a smooth transition to air. The width of this transition is a direct indication for the roughness of the polymer film (Figure 1B). The SLD profile of the PHEMA brush postmodified with D-10 leucine reveals an abrupt transition at the silicon oxide−brush interface followed by a gradual increase and reaches a maximum at the top of the polymer brush layer (Figure 1D). The increase in the SLD with increasing distance from the silicon substrate reflects the D-10 leucine concentration gradient in the brush, going from a pure PHEMA brush near the silicon−brush interface to a D-10 leucine-rich PHEMA brush at the top layer. The data in Figure 1 indicate that the NPC mediated postpolymerization modification of a 1016 Å thick PHEMA brush with D-10 leucine does not result in quantitative conversion of the hydroxyl side-chain functional groups. The fit of the reflectivity data indicates that a high concentration of D-10 leucine is only found in the top ∼285 Å of the brush. In between these extremes, the concentration of D-10 leucine increases gradually with increasing distance from the silicon substrate. Comparison of the experimentally determined SLD of the postmodified PHEMA and the theoretical value for D-10 leucine modified PHEMA suggests a maximum conversion at the top of the layer of ∼73%. The reflectivity data in Figure 1C,E were fitted with a 5-layer model: bulk-Si/SiO_2/PHEMA/postmodified PHEMA/air. A 10-layer model that takes into account a concentration gradient of deuterated molecules within the polymer brush was also evaluated; however, the final distribution profiles were found to be similar to those obtained with the 5-layer model. Furthermore, the χ^2 parameter was smaller, i.e. the quality of the fit better, for the 5-layer model as compared to the 10-layer model. For the remainder of this article, the 5-layer model has been used to describe the distribution of deuterated amino acids within the PHEMA brushes.

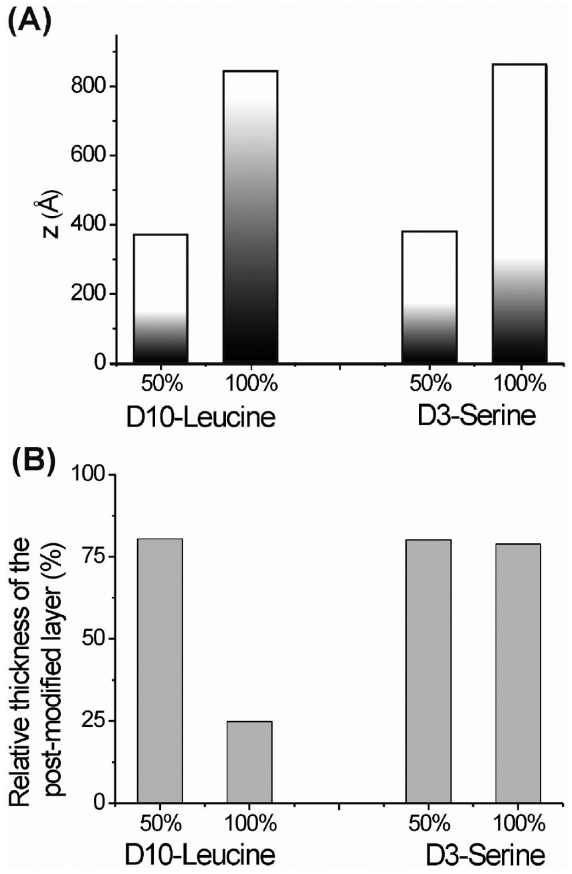


Figure 4. Influence of the nature of the amino acid on the postpolymerization modification of poly(2-hydroxyethyl methacrylate) brushes of various grafting densities. (A) Total thickness (bars) and thickness of the postmodified layer (top white area) for brushes of different grafting densities modified with D-10 leucine and D3-serine. (B) Relative thickness of the postmodified layer for PHEMA brushes of different grafting densities for the two investigated amino acids.

Figure 2 summarizes the results of neutron reflectometry experiments that were carried out on dense PHEMA brushes (i.e., grown from substrates modified with 100% of the ATRP active chlorosilane) of four different initial thicknesses (100, 200, 410, and 880 Å) after postpolymerization modification with D-10 leucine. Independently of the brush thickness, it was found that the postpolymerization modification conditions applied here only resulted in functionalization of the top ∼200 Å layer (Figure 2B). The gray shading in Figure 2A (black: unmodified PHEMA; white: maximum conversion of hydroxyl groups) is a visual representation of the concentration gradient of deuterated groups in the brush as obtained from the experimental SLD profile (see e.g. Figure 1D).

Figure 3 illustrates the influence of grafting density on the postpolymerization modification of PHEMA brushes with D-10 leucine. Brushes of different grafting densities (25%, 50%, 75%, and 100% of active initiator) and with initial thicknesses of 70, 200, 250, and 880 Å, respectively, were activated with NPC and further reacted with D-10 leucine. The polymer brushes that were used to obtain the data shown in Figure 3 were all prepared with the same polymerization time and as a consequence consist of polymer chains of comparable degrees of polymerization. Whereas for the densest brushes the thickness of the postmodified layer, i.e. the conversion of PHEMA side-chain hydroxyl groups, accounts for ∼25% of the total brush thickness, ∼68% of the total film thickness is postmodified when the brush density is decreased to 75%. Further decreasing the grafting density from 75% to 50% or 25% leads to a slight increase in the relative thickness of the postmodified layer (viz. an improvement in conversion) to 74% and 81%, respectively. Since the postpolymerization modification reactions were conducted in good solvents for the surface-tethered PHEMA chains, the increase in overall conversion with decreasing grafting density is probably due to the enhanced accessibility of the polymer brush layer with decreasing grafting density.

All the postpolymerization modification experiments discussed so far have been carried out with D-10 leucine. To investigate the possible influence of the structure and chemical composition of the amino acid reagent on the postpolymerization modification, additional experiments were carried out with D-3 serine. Figure 1E shows the experimental reflectivity profile recorded on a PHEMA brush after postpolymerization modification with D-3 serine. The corresponding SLD profile (Figure 1F) shows a rapid increase as the distance from the Si surface increases, and the maximum SLD value is reached after a distance of ∼250 Å from the surface. This result is in contrast with the one obtained when the reaction was performed with D-10 leucine, in which case the SLD increased slowly and reached a maximum only at the vicinity of the top of the polymer layer (Figure 1D). Figure 4 compares the postpolymerization modification of PHEMA brushes of different grafting densities with D-10 leucine and D-3 serine. The results summarized in Figure 4 were obtained using PHEMA brushes of the same initial thickness and density, which were activated with NPC and subsequently exposed to a 1 mM solution of D-10 leucine and D-3 serine (100% density, initial thickness 880 Å; 50% density, initial thickness 200 Å) The data in Figure 4 clearly illustrate that the extent to which postpolymerization modification proceeds depends on the nature of the amino acid. For a dense brush, the thickness of the postmodified layer was 3 times larger when D3-serine was used instead of D-10 leucine. Whereas decreasing the brush density led to a strong increase in hydroxyl side-chain modification in case of D-10 leucine, the relative thickness of the D3-serine postmodified top layer of the PHEMA brush did not significantly vary with brush density. Comparison of the experimental and the theoretical SLD of D-3 serine postmodified PHEMA suggests a degree of conversion at the rim of the layer of ∼77%. The results in Figure 4 reflect the differences in size and polarity between D-10 leucine (bulky and apolar) and D-3 serine (smaller and more polar than leucine) and the ability of these amino acids to penetrate the activated PHEMA brushes.

When investigating the postpolymerization modification of PHEMA brushes with D-10 leucine and D-3 serine, it is important to realize that the observed results do not necessarily only reflect the size and polarity of the amino acid and steric crowding of the polymer brush but may also be due to nonhomogeneous NPC activation, i.e. the presence of NPC concentration gradients throughout the brushes. To study the presence of possible NPC concentration gradients, activated PHEMA brushes were analyzed with FTIR and UV−vis spectroscopy. FTIR spectra of the NPC activated brushes still revealed the presence of an OH vibration around 3500 cm^{-1}, indicating incomplete hydroxyl group conversion (see Supporting Information Figure S1). The influence of brush thickness and grafting density on the NPC activation was investigated by monitoring the UV absorbance of a series of activated PHEMA

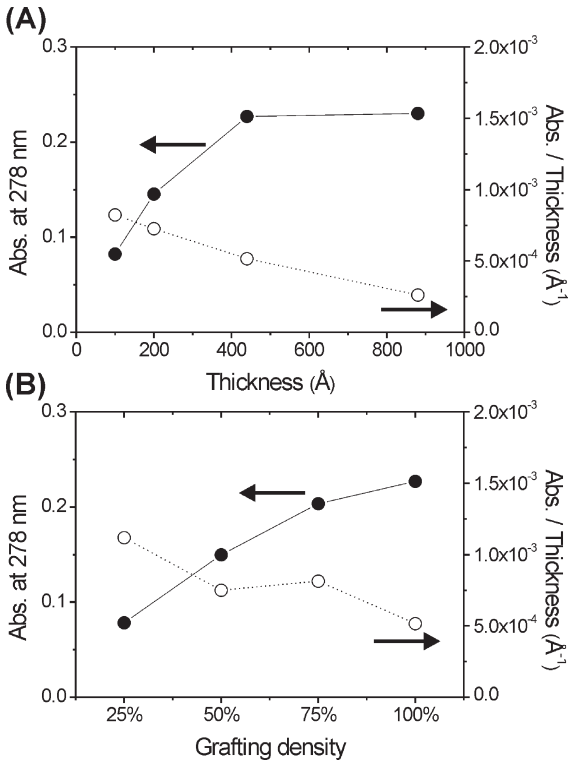


Figure 5. Intensity (●, left) and normalized intensity (○, right) of the UV absorbance band of (A) NPC-activated PHEMA brushes of different thickness and a grafting density of 100% and (B) NPC-activated brushes of different density (polymerization time 2 h).

brushes with increasing brush thickness (Figure 5). For thin PHEMA brushes (up to 400 Å), the absorbance at 278 nm was found to increase almost linearly (Figure 5A). After that, a plateau value was reached. When the absorbance is normalized with respect to the brush thickness, however, a continuous decrease in intensity with increasing brush thickness is observed, which suggests that NPC activation is nonhomogeneous and predominantly occurs at the top layer of the brush. UV−vis analysis of a series of brushes of different grafting densities (but prepared with an identical polymerization time) revealed a continuous increase in the UV−vis absorbance at 278 nm but a continuous decrease in the normalized (with respect to thickness) UV−vis absorbance with increasing brush density (Figure 5B). These results reflect the increased accessibility of the side-chain hydroxyl groups with decreasing grafting density. Taken together, the data in Figure 5 indicate that postpolymerization modification of PHEMA brushes with D-10 leucine and D-3 serine is the result of a complex interplay of effects of steric crowding by the surface grafted polymer chains, size, and polarity of the amino acid as well as possible surface energy differences between the amino acids and NPC activation gradients.

■ CONCLUSIONS

This contribution has investigated the distribution of functional groups in polymer brushes obtained via NPC-mediated postpolymerization modification with deuterated amino acids. Neutron reflectometry experiments revealed that for dense PHEMA brushes postpolymerization modification with D-10 leucine is restricted to the top ∼200 Å of the layer regardless of the brush thickness. Decreasing the grafting density from 100% to 75% or less significantly increased the extent of postpolymerization modification and results in brushes in which 75% of the total thickness is postmodified with D-10 leucine. Experiments with D-3 serine demonstrated that the nature of the amino acid also plays a role; postpolymerization modification with this nonhydrophobic and sterically less demanding amino acid resulted in polymer brushes that were postmodified for 77% independently of brush density. In addition to brush thickness and density and the nature of the amino acid, UV−vis absorbance studies revealed that a nonuniform NPC activation also contributes to a nonhomogeneous postpolymerization modification of the PHEMA brushes. For dense brushes, the NPC density was high near the brush−air interface but decreased with increasing brush thickness. Furthermore, at equivalent polymerization times, lower density brushes were activated to a larger extent than the former, which reflects the difference in accessibility. The results described in this article may be valuable not only since they provide guidelines for the preparation of homogeneous functional polymer brushes but also as they point toward the possibility to deliberately, via judicious choice of the reaction conditions, prepare nonuniformly modified polymer brushes, which may possess new and unexpected properties.

■ ASSOCIATED CONTENT

Supporting Information. FTIR spectra of PHEMA and NPC-activated PHEMA brushes. This material is available free of charge via the Internet at http://pubs.acs.org.

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