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Stimuli-Responsive Interfaces Using Random Polyampholyte Brushes

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ABSTRACT: We study the pH-responsive behavior of random polyampholyte brushes synthesized by surface-initiated Atom Transfer Radical Polymerization. We define the "annealed" polyampholyte as the random copolymer that contains weak acid (methacrylic acid) and weak base (2-(dimethylamino)ethyl methacrylate) units. The "semi-annealed" polyampholyte is defined as the random copolymer that contains the methacrylic acid and a strong base unit (the quaternized amine). The structure of the polyampholyte brushes in aqueous solutions at different pH is determined using neutron reflectivity. The monomer density profile and therefore the brush thickness are obtained. Polymer brushes with various grafting densities are compared. We demonstrate that the structure of the polyampholyte brush depends strongly on the net charge of the chains. With an excess of charge, the brush is as stretched as a polyelectrolyte brush, and the swelling behavior is in good agreement with the scaling laws. At the isoelectric point corresponding to a zero net charge, the polyampholyte effect dominates, resulting in the collapse of the chains. We find that weakly dense polyampholytes have the greatest amplitude of stretching-collapse. We also compare the responsive behavior of the random polyampholyte brushes with that of diblock polyampholyte brushes and mixed polyelectrolyte brushes.

Introduction

Polymer brushes are made of polymer chains densely attached by one end to a surface or interface. They are of great interest in a wide field of industrial and biological applications as well as in academic research. Strategies have been developed for the functionalization of surfaces with polymer brushes to realize smart surfaces with responsive and adaptative properties. They can also be exploited to generate micropatterned polymer monolayers.[1−23]

Polyampholytes are ionic polymers that contain both positively and negatively charged groups.[4−6] Synthetic copolymers as polyampholytes are made of monomer units with acid and base groups. If these groups are weak acids or bases, the net charge of the polyampholyte in aqueous solution can be changed by varying the pH. At the isoelectric point, there is an equal number of positive and negative charges on the polyion, resulting in a zero net charge. Around the isoelectric point, the polymers exhibit the properties of polyampholytes. The ion pairing between the oppositely charged groups in the same chain or neighbor chains leads to a collapsed state. At high charge asymmetry, far above or below the isoelectric pH, the polymers behave as polyelectrolytes because of an excess of charge (positive at low pH and negative at high pH). Most of polyampholytes exhibit an interesting transition between stretching and collapse conformations, which could be exploited as stimuli-responsive properties in response to the pH.

In brushlike systems, the conditions required are that the chains are connected irreversibly to the surface of the substrate and the distance between anchoring points is small enough to induce significant chains stretching. Brushlike systems could be obtained from amphiphilic block copolymers spread at the air−water interface or adsorbed on a solid substrate. But these systems have the constraints of physisorption, namely thermal and solvolytic instability. Polymer brushes in which the chains are covalently bound to the surface of a solid substrate are often preferred though they are more difficult to prepare. So far there are only a few studies on polyampholyte brushes and none on random polyampholyte brushes. There have been a few experimental works conducted on diblock polyampholyte brushes and also on comparable systems such as mixed polyelectrolyte brushes.

Minko and co-workers have extensively investigated binary polymer brushes in which two different polymers are randomly grafted to the same substrate.[3−8] They have synthesized mixed polyelectrolyte brushes with two oppositely charged weak polyelectrolytes via the "grafting to" approach. The pair of homopolymers was poly(acrylic acid) (PAA) and poly(2-vinylpyridine) (P2VP).[9] They demonstrated that the pH signal might be used to switch the wetting behavior and the swelling behavior of the mixed polyelectrolyte brush. They proposed that at pH values below (above) the isoelectric point the mixed brush acted as a polyelectrolyte brush in which the top was occupied by the positively (negatively) charged stretched P2VP (PAA) chains.

Brittain's group have utilized atom transfer radical polymerization with the "grafting from" strategy to synthesize diblock copolymer brushes.[10−13] Recently, they investigated polyampholyte brushes such as poly(acrylic acid-*b*-vinylpyridine)[14] and poly(2-(dimethylamino)ethyl methacrylate)-*b*-acrylic acid)[15] diblock copolymers. They demonstrated that these diblock polyampholyte brushes responded to stimuli such as pH and electrolyte concentration, showing both polyelectrolyte and polyampholyte effects. Plotting the curve of the film thickness as a function of the pH, they observed a "U"-shaped trend with a minima centered at the isoelectric point. The Huck group is also interested in switchable surfaces of block polymer brushes.[16,17] In particular, they synthesized triblock polymer brushes containing poly(2-(methacryloyloxy)ethyl)trimethylammonium chloride, poly(methyl methacrylate), and poly(methacrylic acid) blocks using surface-initiated aqueous atom transfer radical polymerization.[18] Poly(2-(dimethylamino)ethyl methacrylate)-*b*-acrylic acid) diblock copolymer brushes were investigated by Bhat et al.[19] They observed a decrease in the thickness of the polymer brush around the isoelectric point. Yu et al.[20] synthesized by ATRP oppositely charged weak polyelectrolyte block copolymer brushes composed of poly(2-vinylpyridine) (P2VP) and poly(acrylic acid) (PAA) with different block length. They demonstrated that the wetting property of the P2VP-*b*-PAA could be regulated by pH

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reversibly. The changes of surface chemical composition and surface roughness and the wetting behavior illustrated the surface rearrangement occurred during the treatment of the P2VP-*b*-PAA in aqueous solutions with various pH values. In summary, all these studied block polyampholyte brushes have shown stimuli-responsive properties with pH, as expected. They could also have various morphologies depending on the ratio of the block lengths.

Shusharuna and Linse[21] performed mean-field lattice theory calculations of a diblock polyampholyte grafted onto an uncharged planar surface. They studied the effect of varying the polyelectrolyte charge and length and the concentration of added salt on the brush structure. They proposed that the balance between electrostatic repulsions of like charges and attractions of opposite charges should lead to a variety of possible chain conformations including a coexistence of stretched and coiled chains. Monte Carlo simulations[22] have also been used with lattice mean-field theory to examine diblock polyampholytes grafted on spherical particle. They found that the structure of the polyampholyte brush depended strongly on the charge of the inner block. In the polyelectrolyte limit with uncharged inner block, the chains are stretched and form a polyelectrolyte brush. In the limit of a polyampholyte with zero net charge, the chains are collapsed and form a polyelectrolyte complex with entangled chains. At intermediate charge compensation, stretched and collapsed chains coexist.

In addition, Stamm and co-workers have investigated the adsorption of the ampholytic diblock copolymer poly(2-(dimethylamino)ethyl methacrylate)-*b*-methacrylic acid) from dilute aqueous solutions on silicon substrates.[23−27] The amount of the adsorbed layer and the lateral morphology have been determined as functions of the copolymer chain length and composition, the pH of the solution, and the salt concentration. They demonstrated a strong dependence on the net charge of the diblock. In particular, the adsorbed amount reached its maximum at the isoelectric point of the polyampholyte.

We have been exploring the pH-responsive behavior of annealed polyions at interfaces. Recently, we have investigated the adsorption of randomly annealed polyampholytes with various molar ratios from dilute aqueous solutions.[28] We have also reported the swelling behavior of weak polybase brushes.[29] It has been shown that their swelling behavior was in good agreement with the scaling laws predicted by mean-field theories.[30−40] In addition, the variation of the effective charge ratio of the weak polybase brush with pH could be deduced from the scaling laws. Here, we are interested in the stimuli-responsive behavior of random polyampholyte brushes. We define the “annealed” polyampholyte as the random copolymer that contains a stoichiometric molar ratio of methacrylic acid (MAA) and (2-(dimethylamino)ethyl methacrylate) (DMAEMA). In that case, both units are annealed (weak acid and weak base). We define the “semi-annealed” polyampholyte as the random copolymer that contains a stoichiometric molar ratio of weak acid units (MAA) and strong base units (quaternized DMAEMA). In that case, the “semi-annealed” polyampholyte consists of the mixture of annealed (weak acid) and quenched (strong base) segments. The synthesis of the random polyampholyte brushes, which has been reported in a previous article,[41] will be briefly recalled in this paper. We will show the structure of the random polyampholyte brushes investigated by neutron reflectivity. This surface technique allows the determination of the monomer density profile and therefore the computation of the brush thickness in aqueous solution, varying the pH. We will also study the effect of the grafting density of the brush. Finally, we will compare the pH-responsive behavior of the random polyampholyte brushes with that of block polyampholyte brushes and mixed polyelectrolyte brushes.

Experimental Section

Chemical Products and Silicon Substrates. 2-(Dimethylamino)ethyl methacrylate (DMAEMA, Aldrich, 98%), *tert*-butyl methacrylate (^{t}BuMA, Aldrich, 98%) triethylamine (Aldrich, 99.5%), and solvents such as dimethylformamide (DMF, SDS, 99%) and tetrahydrofuran (THF, SDS, 95%) were passed through a column of activated basic alumina and degassed with high-purity nitrogen prior to use. Copper(I) bromide (CuBr) (Aldrich 98%) was purified as described in the literature. Dimethylchlorosilane (Roth Sochiel, 98%), chlorododecyldimethylsilane (Aldrich, 95%), 10-undecen-1-ol (Aldrich, 98%), 2-bromoisobutyryl bromide (Aldrich, 98%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich, 97%), ethyl 2-bromoisobutyrate (Et2Br^{i}Bu, Aldrich, 98%), anhydrous tetrahydrofuran (THF, Aldrich, 99.9%), and anhydrous toluene (Aldrich, 99.8%) were used as received.

Silicon wafers were purchased from ACM. $100 \times 50 \times 10$ mm^3 monocrystals were used for neutron reflectivity measurements. Silicon substrates were cleaned by treatment with freshly prepared “piranha” solution (70:30 v/v concentrated H_2SO_4/30% aqueous H_2O_2) at 150 °C for 30 min. The substrates were then rinsed with pure water (Millipore, resistivity = 18.2 MΩ·cm), cleaned by ultrasound in water for 1 min, and dried under nitrogen.

Synthesis of Polymer Brushes. The synthesis of polymer brushes was reported in a previous paper.[41] The experimental procedure for the formation of P(DMAEMA-*st*-^{t}BuMA) brushes and subsequent in situ conversion into P(DMAEMA-*st*-MAA) and P(TMAEMA-*st*-MAA) polyampholyte brushes are outlined in Scheme 1.

The surface-attachable initiator was synthesized following the same strategy used by Matyjaszewski et al.[42] and Husseman et al.[43] Briefly, (11-2-(2-bromo-2-methyl)propionyloxy)undecyldimethylchlorosilane was obtained after the esterification of 10-undecen-1-ol with 2-bromo-isobutyryl bromide and the hydrosilylation with dimethylchlorosilane. The initiator was covalently grafted on silicon substrates by a self-assembling technique. The P(DMAEMA-*st*-^{t}BuMA) copolymer brush was generated from the substrate by atom transfer radical polymerization. The free initiator ethyl-2-bromoisobutyrate was added to the polymerization to provide an overall concentration of ester in the polymerization mixture, which controls the chain growth of both the surface-attached and bulk initiators. The copolymer brushes were characterized using ellipsometry by measuring the dry thickness γ (Å). The grafting density, σ, which corresponds to the number of chains per unit area, was calculated from the dry thickness γ and the molecular weight M_n by

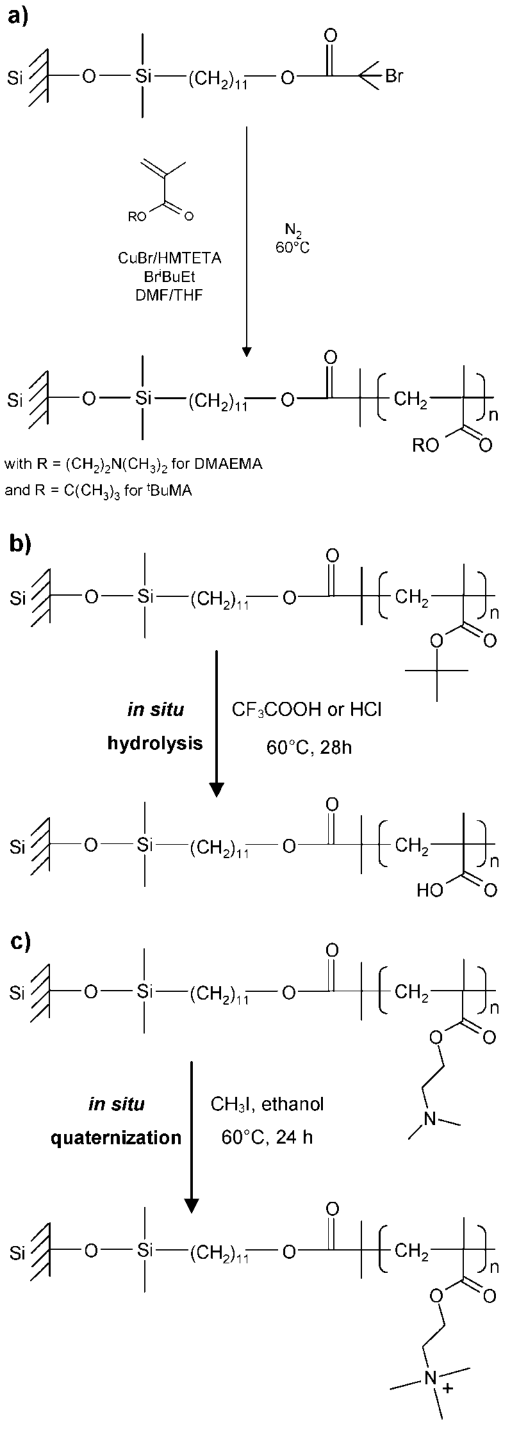
$$\sigma = \frac{\gamma d N_A}{M_n} \tag{1}$$

where d is the mean density of P(DMAEMA-*st*-^{t}BuMA) copolymer ($d = 1.17$ g/cm^3) and M_n is the molecular weight of the copolymer ($M_n = 67\,000$ g/mol).

The conversion of ^{t}BuMA units into MAA units was performed by acid hydrolysis. A total hydrolysis reaction of the copolymer brushes (with a minimum degrafting of polymer chains) was obtained by heating 1.1 mol/L of a trifluoroacetic acid solution at 60 °C for 28 h. The quaternization reaction of DMAEMA units was performed with methyl iodide in ethanol. A complete quaternization reaction without any chain degrafting, was observed after 24 h at a temperature of 60 °C. FTIR-ATR spectrometry was used to characterize the chemical conversion of the copolymer brush and in particular to control that the hydrolysis and quaternization reactions were fully successful.

Neutron Reflectivity. Neutron reflectivity measurements were performed at the silicon−liquid interface on the reflectometer EROS at the Laboratoire Léon Brillouin, CEA-Saclay, France. The experimental procedure and setup were described in detail in previous papers.[28,29] Let us precise that neutron reflectivity measurements were performed with protonated polymer brushes

Scheme 1. (a) Synthesis of Random Copolymer Brushes Using Surface-Initiated Atom Transfer Radical Polymerization (ATRP),[a] (b) Conversion of the Ester Group (^{t}BuMA) into Methacrylic Acid (MAA) by an in Situ Hydrolysis Reaction, and (c) Conversion of the Annealed (DMAEMA) Units into the Quenched 2-(Trimethylamino)ethyl Methacrylate (TMAEMA) Units by an in Situ Quaternization Reaction



[a] The monomer units are 2-(dimethylamino)ethyl methacrylate (DMAEMA) and *tert*-butyl methacrylate (^{t}BuMA).

and deuterated water in order to determine the monomer density profile of the brushes.

Neutron reflectivity is sensitive to the scattering length density profile perpendicular to the interface $\rho(z)$. A reliable model-independent method was chosen to determine $\rho(z)$. The brush was modeled as a set of layers, each characterized by a fixed thickness and a scattering length density. Two adjacent layers were connected using error functions of fixed width to get a continuous profile. The procedure consisted of choosing a scattering length density profile and finding the corresponding parameters for which the calculated reflectivity curve fits the best the experimental reflectivity data. This reliable method allowed the determination of a continuous scattering length density profile without making any assumption about its analytical form.

The monomer volume fraction profile $\phi(z)$ was then deduced from $\rho(z)$. $\gamma = \int_0^\infty \phi(z)\,dz$ is an important parameter because it is independent of the shape of $\phi(z)$. It corresponds to the thickness of the dry layer and can be measured by another technique such as ellipsometry. The swollen thickness, L (Å), was determined by computing the normalized first moment of the monomer density profile $\phi(z)$.

Results and Discussion

Synthesis and Characterization of Polyampholyte Brushes. The synthesis and characterization of the brushes have been described in detail in a previous paper.[41] The P(DMAEMA-*co*-^{t}BuMA) copolymer brush was synthesized by surface-initiated atom transfer radical polymerization.[44,45] The grafting density varied from 0.1 to 0.35 nm^{-2} with the molecular weight, M_n, and the polydispersity of the polymer chains equal to 67 000 g/mol and 1.4, respectively. It was also shown that the copolymer was randomly distributed with a stoichiometric molar proportion of DMAEMA and ^{t}BuMA. The characterization of polymer chains (molecular weight, polydispersity, and microstructure) was performed on free chains obtained in bulk by adding free initiators. Considering previous works, we assumed that the characteristics of surface-attached and bulk polymer chains were the same. The ^{t}BuMA was converted into MAA by a hydrolysis reaction. The DMAEMA could be quaternized to a strong base (TMAEMA), which is not pH-sensitive. Using FTIR-ATR, we demonstrated that the hydrolysis and the quaternization reactions were successful to obtain P(DMAEMA-*st*-MAA) and P(TMAEMA-*st*-MAA) brushes.[29] Contrary to the nonaggressive quaternization reaction, the acid hydrolysis could lead to a cleavage of chains at the siloxane anchoring site. Yet, the real challenge of this work was not to keep the same grafting density for converted brushes, but to form polyampholyte brushes of the same chain length and various grafting densities in the projection of structural investigation.

The ampholytic copolymers were also characterized by acid/base titration using polymer solutions at 1 g/L and 0.1 mol/L NaOH solution. From the titration curves, we determined the dissociation constants of the weak acid and base and the variation of the fractions of each unit with pH. Figure 1 shows the fractions of positively charged units, f^{+}, and negatively charged units, f^{-}, versus pH for P(DMAEMA-*st*-MAA) and P(TMAEMA-*st*-MAA) copolymers. Also is shown the net charge or global charge $\Delta f = f^{+} - f^{-}$. The net charge is less than 0.4 for P(DMAEMA-*st*-MAA) in a pH range between 6.0 and 7.6 and for P(TMAEMA-*st*-MAA) at pH > 6.0. It was also observed that the solution was turbid in the pH range of low net charge. The turbidity of the solution is due to the attraction between oppositely charged units with equal ratio, resulting in the formation of aggregates. These observations were in agreement with other studies on the solubility of polyampholytes. The insolubility occurs around the neutral point for random and diblock polyampholytes, in contrary to alternating polyampholytes, which are usually soluble over the entire range of pH and in particular at the isoelectric point.[4] In addition to titration measurements, it was demonstrated by ^{13}C NMR spectroscopy that polyampholyte chains were random copolymers containing acid and base units in a stoichiometric molar ratio. Anyway, a random distribution along the chain was expected for the radical copolymerization of like methacrylate monomers such as DMAEMA and ^{t}BuMA. As shown by

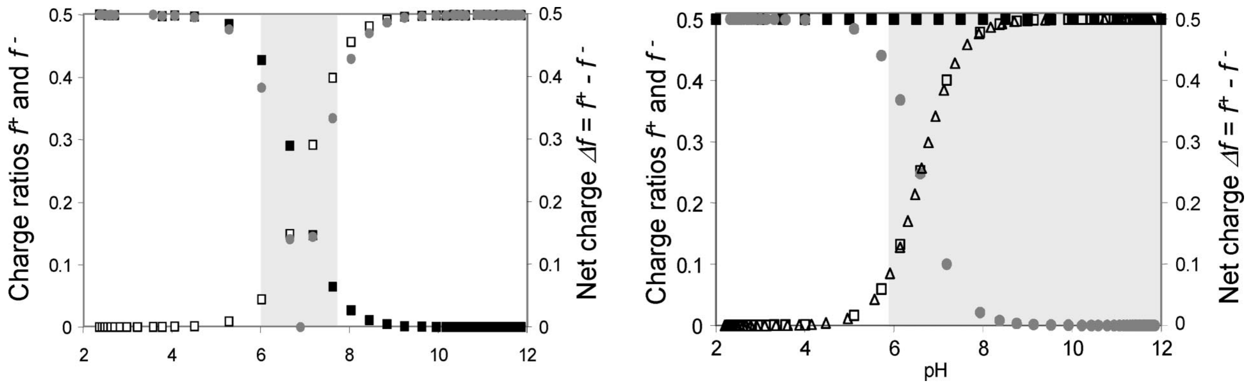


Figure 1. Fractions of positively charged units f^+ (■), negatively charged units f^- (□) and net charge (or global charge) $\Delta f = f^+ - f^-$ (●) as functions of the pH. The variation of f^+ and f^- with the pH was determined from acid/base titration curves. The date are shown for P(DMAEMA-*st*-MAA) (left) and P(TMAEMA-*st*-MAA) (right). Also is shown the variation of the charge ratio for the PMAA homopolymer (△). The turbidity of the polymer solutions is indicated by the gray section.

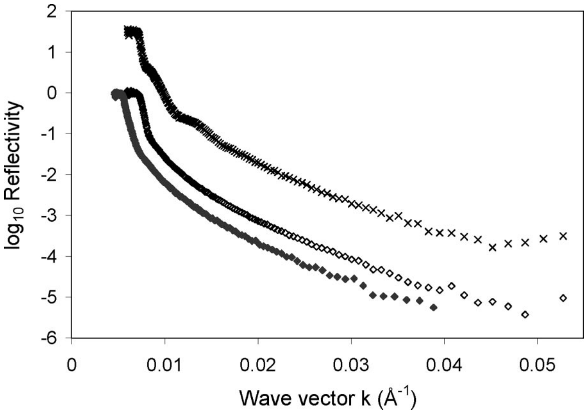


Figure 2. Neutron reflectivity curves of the P(TMAEMA-*st*-MAA) brush ($\sigma = 0.146$ nm^{-2}) in D_2O at pH 2.8 (◊) and pH 5.9 (×) and in a solution of 75:25 v/v D_2O/H_2O at pH 2.8 (♦). The corresponding volume fraction profiles that best fit the experimental data are shown in Figure 3.

Miranda et al.,[46] the relative reactivity ratios are 0.97 for DMAEMA and 1.26 for ^{t}BuMA.

"Semiannealed" Polyampholyte Brushes. "Semiannealed" polyampholyte brushes are P(TMAEMA-*st*-MAA) brushes containing a stoichiometric molar ratio of quenched units (TMAEMA) and weak acid units (MAA). The swelling behavior of polyampholyte brushes was investigated using neutron reflectivity.

Figure 2 shows neutron reflectivity curves of the P(TMAEMA-*st*-MAA) brush with the grafting density $\sigma = 0.146$ nm^{-2} at pH 2.8 and pH > 5.9 (all the reflectivity curves at pH higher than 5.9 were the same). For pH > 5.9, the reflectivity curves display obvious Kiessig franges, indicating that the brush is contracted with an abrupt profile. In the neutron reflectivity curve at pH 2.8, there is a lack of Kiessig franges. This might be attributed to either a highly extended density profile or a contrast matching of the scattering length density of the polyampholyte and the silicon substrate. In the second assumption, the density profile of the polyampholyte brush might have a step shape, with a volume fraction profile of 0.78, which corresponds to a scattering length density of 2.1×10^{-6} Å^{-2} (the same as for silicon). In that case, Kiessig franges might be obvious if the neutron reflectivity experiments were performed in a mixture of D_2O and H_2O instead of D_2O. The neutron reflectivity curve of the same polyampholyte brush at pH 2.8 in a solution of 75:25 v/v D_2O/H_2O is displayed in the same figure. Though, the reflectivity curves at pH 2.8 in D_2O and in the mixture D_2O/H_2O show the same monotonous decrease without obvious Kiessig franges. Accordingly, the reflectivity curves of the polyampholyte brush at pH 2.8 correspond to a highly extended density profile.

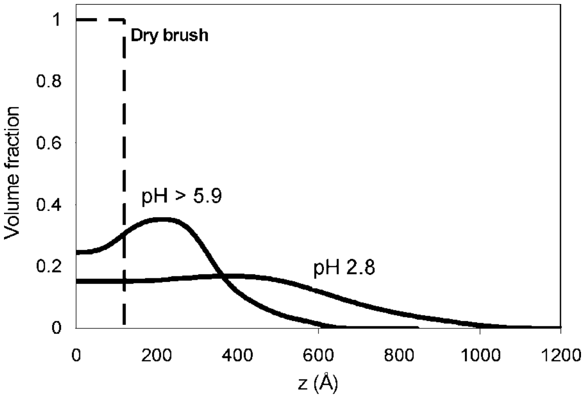


Figure 3. Monomer volume fraction profiles of the P(TMAEMA-*st*-MAA) brush ($\sigma = 0.146$ nm^{-2}) at different pH values. The density profile of the dry brush is also given.

The volume fraction profiles of the "semi-annealed" polyampholyte brushes are displayed in Figure 3 at pH 2.8 and pH > 5.9. They correspond to the best fit of the reflectivity curves. The profile of the dry brush is given as an indication to illustrate that its integral is equal to the dry thickness $\gamma = \int_0^\infty \phi(z)\, dz$. At pH 2.8, the brush is stretched up to 1000 Å from the surface with a density profile that matches with the profile of a polyelectrolyte brush. As expected, the P(TMAEMA-*st*-MAA) brush acts as a polycation brush at low pH values since the TMAEMA quaternized segments are positively charged while the MAA remains as a neutral carboxylic acid unit. The brush collapses at high pH values (pH > 5.9). As the MAA is converted into the carboxylate form, we have a random copolymer that contains an equal ratio of negatively and positively charged segments. A polyampholyte behavior dominates with the formation of complexes between oppositely charged units, resulting in a collapsed conformation of chains. It should be pointed out that the density profile of the collapsed brush is not monotonic. A depletion layer close to the surface was observed. The denser region next to the solvent might be a hydrophobic zone due to the complexation of oppositely charged units. This barrier-like zone might be glassy. It might prevent from a collective ionization of the whole brush, resulting in a limited collapse of the polyampholyte brush.

The swollen thickness that is the mean thickness of the brush within solvent was deduced from the volume fraction profile. It was determined in function of the pH for various grafting

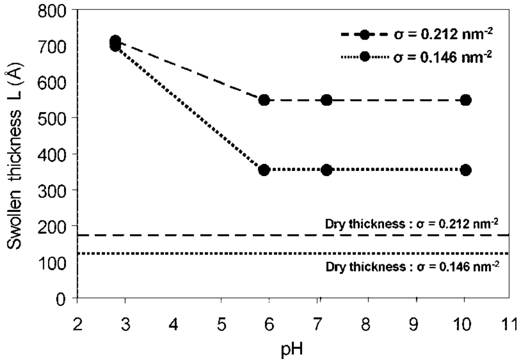


Figure 4. Swollen thickness L vs pH for two P(TMAEMA-*st*-MAA) brushes of various grafting densities. The dry thickness is also given.

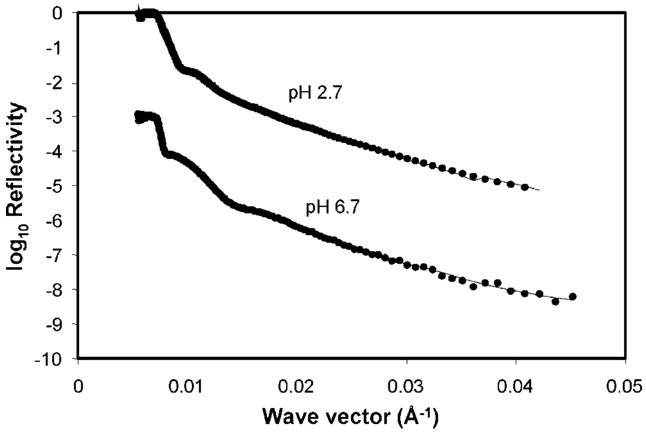


Figure 5. Neutron reflectivity curves of the P(DMAEMA-*st*-MAA) brush (σ = 0.132 nm^{-2}) at different pH values. The best fits of the experimental data are shown by solid lines.

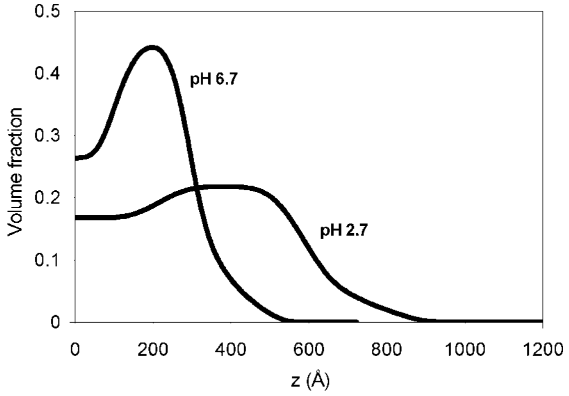


Figure 6. Monomer volume fraction profiles of the P(DMAEMA-*st*-MAA) brush (σ = 0.132 nm^{-2}) at different pH values. The corresponding reflectivity curves are shown in Figure 5.

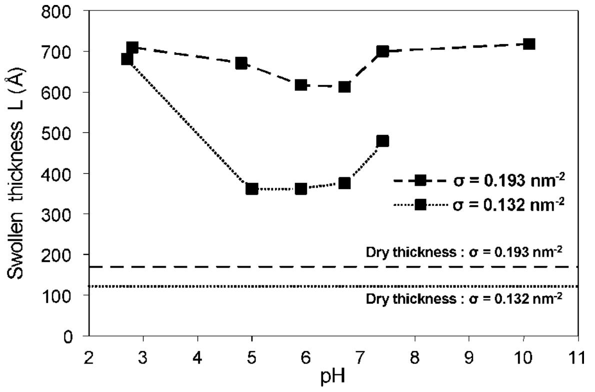


Figure 7. Swollen thickness L vs pH for two P(DMAEMA-*st*-MAA) brushes of various grafting densities. The dry thickness is also given.

densities (Figure 4). At low pH values (pH 2.8), the swollen thickness has the same value for both grafting densities ($L \sim$ 700 Å), as expected for polyelectrolyte brushes with the same chain length. The comparison with polyelectrolyte brushes will be discussed further in this paper. The swollen thickness remains constant for pH > 5.9, which was the pH range of low net charge as shown by titration measurements. The thickness is the lowest for the least dense polyampholyte brush. These results indicate the collapse in the pH range of neutral charge is significant for the weakly dense brush.

"Annealed" Polyampholyte Brushes. "Annealed" polyampholyte brushes are P(DMAEMA-*st*-MAA) brushes containing a stoichiometric molar ratio of weak base (DMAEMA) and weak acid units (MAA). The neutron reflectivity curves of the P(DMAEMA-*st*-MAA) brush with a grafting density equal to 0.146 nm^{-2} at pH 2.7 and pH 6.7 are shown in Figure 5. For pH 6.7, the reflectivity curve displays more obvious Kiessig franges with a higher period, suggesting that the brush is more collapsed than at pH 2.7. Figure 6 displays the volume fraction profiles corresponding to the best fits of these data. At pH 2.7, the density profile of the "annealed" polyampholyte brush is comparable to that of a polyelectrolyte brush, and the chains extended to 900 Å from the surface. The polyampholyte brush acts as a polyelectrolyte brush at low pH values since the DMAEMA is ionized and the MAA is neutral, resulting in an excess of charge. At pH 6.7, the "annealed" polyampholyte is globally neutral given that it contains both ionized DMAEMA and MAA units, leading to a collapsed brush. As observed for the "semi-annealed" brush, the density profile is not monotonic. There are a depletion layer close to the surface and a glassy barrier-like zone at the side of the solvent. The swollen thickness of the "annealed" brush was determined at various pH for two different grafting densities (Figure 7). The pH range of the brush collapse (between 6.0 and 7.6) corresponds to the isoelectric region obtained by titration measurements. The swollen thickness is the same for both grafting densities at pH 2.7 where the polyampholyte brush acts as a polyelectrolyte brush. In the pH range of low net charge, the less dense brush is significantly more collapsed.

Comparison with Polyelectrolyte Brushes. We compared the swelling behavior of the polyampholyte brushes with that of the corresponding polyelectrolyte brushes (PDMAEMA and PMAA homopolymers). The P(DMAEMA-*st*-MAA) brush was expected to act as a polyelectrolyte brush at low and high pH values. At low pH, the MAA units are neutral and the DMAEMA is fully ionized. The MAA is charged while the DMAEMA remains neutral for high pH. As the quaternized TMAEMA units are positively charged in the whole pH range, the P(TMAEMA-*st*-MAA) brush might act as a polyelectrolyte brush at low pH values.

In Figure 8, the swollen thickness of the "annealed" and "semi-annealed" polyampholytes brushes and the PDMAEMA brush at low pH is shown as functions of the polymerization degree N. The data can be best fitted by an affine law with the same slope equal to 1.52. These results clearly demonstrate that the polyampholyte brushes are polyelectrolyte brushes at low pH values. Actually, the scaling law of the swollen thickness of the polyelectrolyte brush in the osmotic regime is given by $L \propto Na\alpha^{1/2}$ with a being the monomer size and α being the effective charge ratio.[33] The slope of the affine straight line L vs N is equal to the product $ka\alpha^{1/2}$ with $k = (8/(3\pi^2))^{1/2}$.[35] As all the data can be fitted by the same straight line, the factor

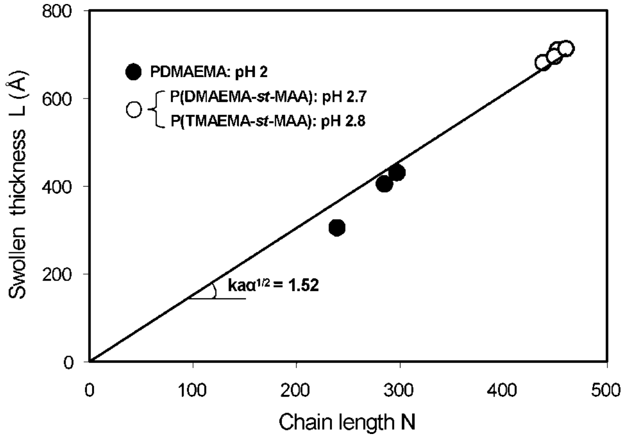


Figure 8. Swollen thickness L vs polymerization degree N for the PDMAEMA, P(DMAEMA-*st*-MAA), and P(DMAEMA-*st*-MAA) brushes at low pH. The slope of the affine law that best fits the data is equal to 1.52.

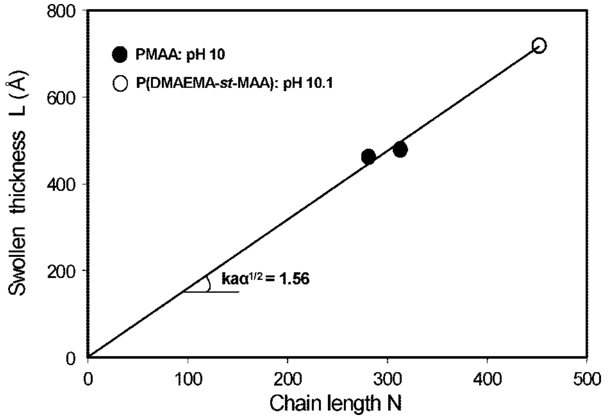


Figure 9. Swollen thickness L vs polymerization degree N for the PMAA and P(DMAEMA-*st*-MAA) brushes at high pH. The slope of the affine law that best fits the data is equal to 1.56.

$ka\alpha^{1/2}$ is the same for the PDMAEMA homopolymer and the "annealed" and "semi-annealed" copolymers brushes. It follows that the effective charge ratio is equivalent for the three brushes if the monomer size is supposed to be identical.

The same analysis was applied for the P(DMAEMA-*st*-MAA) and the PMAA brushes at high pH (Figure 9). It turns out that the PMAA and P(DMAEMA-*st*-MAA) brushes are polyelectrolyte brushes, with the same factor $ka\alpha^{1/2}$. The values of the factor $ka\alpha^{1/2}$ obtained at pH 10 and pH 2 are comparable. These results suggest that the monomer size and the effective charge ratio of all polyelectrolyte brushes used in this study (PMAA and PDMAEMA homopolymers, P(TMAEMA-*st*-MAA), and P(DMAEMA-*st*-MAA) copolymers) are equivalent.

We also studied the pH-responsive properties of the polyampholyte and the polyelectrolyte brushes in terms of deformation amplitude. The deformation amplitude was defined as the ratio of the swollen thickness at the pH corresponding to the maximum of the chains stretching and the swollen thickness at the pH corresponding to the maximum of the chains collapse. For the DMAEMA brushes, the deformation amplitude is the ratio between the values at pH 2 (the polybase brush acts as a strong polyelectrolyte brush) and at pH 10 (the PDMAEMA brush is considered as a neutral polymer brush). For the polyampholyte brushes, the maximum of the chains stretching corresponds to the polyelectrolyte brush regime and the chains collapse occurs for globally neutral polyampholytes (pH more than 5.9 for the semi-annealed polyampholyte and pH between 6.0 and 7.6 for the annealed polyampholyte, as shown previously). The variation of the deformation amplitude with the grafting density is displayed in Figure 10. The variation is quite weak for the PDMAEMA brush. This is not surprising given that the PDMAEMA brush varies from a polyelectrolyte brush to a neutral polymer brush. In any case, the brush remains in a good solvent. For the polyampholyte brushes, the deformation amplitude increases highly with decreasing grafting densities. These results might be attributed to a weak collective ionization of the globally neutral polyampholyte chains for highly dense brushes, resulting in a limited collapse. A sparse brush might be likely to act as single chains which acid and base segments would be fully ionized at the isolectric point. The partial ionization of the polyampholyte brushes might also explain the slight difference of the deformation amplitude between the annealed and semi-annealed polyampholyte brushes. For the annealed polyampholyte, both acid and base segments have to be ionized in comparison with only MAA units for the semi-annealed polyampholyte. As suggested previously, the partial ionization of the polyampholyte brush might be due to the presence of the glassy barrier zone next to the solvent. The density profile of the polyampholyte brushes shows that this barrier zone is larger for denser brushes, leading to a more limited collapse of the brush. This also suggests a pH gradient of the polyampholyte brush in the direction perpendicular to the surface with an inhomogeneous distribution of charges along the chain.

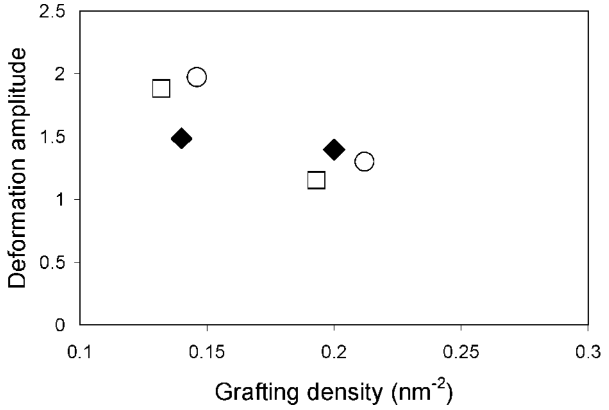


Figure 10. Deformation amplitude of the PDMAEMA brush (◆), the "semi-annealed" (○), and the "annealed" (□) polyampholytes brushes as a function of the grafting density.

Comparison with Mixed Brushes and Diblock Polyampholyte Brushes. We compared the pH-responsive behavior of our random polyampholyte brushes with similar brushes systems. Mixed polyelectrolyte oppositely charged brushes have been investigated by Houbenov et al.[9] The polyanion was poly(acrylic acid), and the polycation was poly(2-vinylpyridine). The average polymerization degree was 350 (328 for PAA and 373 for P2VP), and the dry thickness was 6.4 nm, providing a grafting density close to 0.1 chains/nm^2. The characteristics of the PAA/P2VP mixed brush were quite comparable to those of our random polyampholyte brushes. Figure 11 shows the degree of swelling of the P(MAA-*st*-DMAEMA) brushes and the PAA/P2VP mixed brush. The degree of swelling is the swollen thickness, L, normalized by the dry thickness, γ. As expected, the "U"-shaped trend with a minimum centered about pH 6 was observed for the brushes. The minimum of the U-shaped curve is located at the pH values corresponding to the range of the zero net charge of the brushes. The ion pairing between the protonated amine (or pyridine) groups and dissociated carboxylic acid groups leads to a collapsed state. The degree of swelling of the polyampholyte brush is higher than that of the mixed

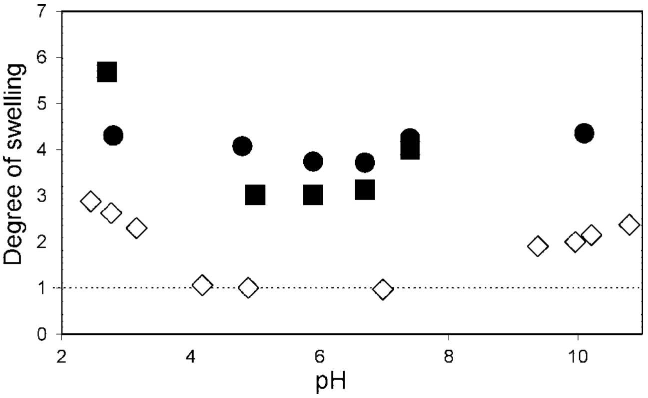


Figure 11. Degree of swelling of polymer brushes vs pH for P(DMAEMA-*st*-MAA) ($\sigma = 0.132$ nm^{-2}, ■), ($\sigma = 0.193$ nm^{-2}, ●), and PAA/P2VP ($\sigma = 0.10$ nm^{-2}, ◇) mixed brush.

polyelectrolyte brush in the whole pH range. At low and high pH values (in the swelling regime), the polyampholyte brushes are twice swollen than the mixed brush. Actually, with an excess of charge, all the polyampholyte chains of the brush are stretched as polyelectrolyte chains. In the mixed brush system, the brush might me divided in two parts. Both homopolymer chains near the surface might adopt a compact conformation on the bottom of the brush while the ionized chains that preferentially occupied the top of the brush stretched away from the surface. The degree of swelling of the polyampholyte brushes was about 3 at the minimum in the "collapse regime". It means that in water the polyampholyte brush remains 3 times more swollen than the dry brush though the polyampholyte is globally neutral. These results indicate that a fraction of water is trapped in the polyampholyte brush. In contrast, the mixed brush was fully collapsed since the swollen thickness measured was equivalent to the dry thickness, suggesting that the water was totally expelled out of the brush. This very strong collapse could be due to the hydrophobic properties of PVP polymers at pH > 4. Strong hydrophobic interactions might amplify the collapsed state of the mixed brush in comparison with our P(MAA-*st*-DMAEMA) brushes. Actually, the mixed brush system is more comparable to the diblock ampholytic copolymer brush studied by Ayres et al.[14] Poly(acrylic acid-*block*-vinylpyridine) diblock copolymer brushes have been prepared. The authors found both polyelectrolyte and polyampholyte effects depending on pH. They observed the familiar U-shaped trend with a gap of 2 orders of amplitude between the lowest and the highest thickness.

It was also interesting to discuss the surface morphologies of these three kinds of brushes. The mixed brushes showed different lateral morphologies depending on the pH. The AFM images displayed some cluster morphologies at the intermediate pH values corresponding to the collapse regime. At low and high pH values, the lateral morphology was rather homogeneous.[3] The same trend has been observed by Yu et al.[20] They have investigated the change of the surface roughness occurred during the treatment of the P(2VP-*b*-AA) brushes by aqueous solution with various pH values. The AFM images showed that the surface fluctuating amplitude and the phase contrast, at the pH values between the isoelectric point of the PAA and P2VP, were about twice higher than the values at low and high pH. For our random polyampholyte brushes, the surface morphologies were almost independent of the pH. Actually, the lateral morphologies obtained by AFM were similar for the swelling and the collapse states. The polyampholyte brushes were rather laterally homogeneous with the surface fluctuating amplitude lower than 1 nm. However, our purpose is not to achieve a detailed study of the surface rearrangement of the polyampholyte brushes. The aim of this discussion is to demonstrate that the polyampholyte brushes had homogeneous surface morphologies at any pH and were then suitable for the characterization by ellipsometry and neutron reflectivity.

Conclusion

We reported the pH-responsive behavior of random polyampholyte brushes. We found that the structure of the brush in aqueous solution was strongly governed by the net charge of the polyampholyte. The brush acted as a polyelectrolyte brush when the chains were globally charged (positively or negatively). For low net charge (at the isoelectric point), the polyampholyte effect dominated resulting in a collapsed brush. Weakly dense polyampholyte brushes had the highest deformation amplitude between the stretching and the collapse states. Actually, a sparse brush might be likely to act as single chains which acid and base segments would be fully ionized at the isoelectric point. The study of these responsive systems is still in progress in our group. We expect these surfaces to show interesting adaptative properties for adsorption and adhesion.

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