Scaling Laws for the Swelling of Neutral and Charged Polymer Brushes in Good Solvents

M. Biesalski[†,§] and J. Rühe*[,†,‡]

Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany, and Institute for Microsystem Technology (IMTEK) Freiburg, University of Freiburg, D-79085 Freiburg, Germany

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ABSTRACT: We compare the swelling of surface-attached neutral poly(4-vinylpyridine) (PVP) and charged poly(*N*-methyl-4-vinylpyridinium iodide) (MePVP) brushes under good solvent conditions using multiple-angle null ellipsometry. The polymer layers were prepared by the "grafting from" technique, where a low molecular mass initiator is self-assembled on the substrate and the polymer brush is grown in situ by free radical chain polymerization. The positively charged MePVP brush was generated from a neutral PVP brush by a polymer-analogous quaternization reaction. As predicted by mean-field theory, the thickness of the neutral swollen brush (PVP) increases with graft density whereas the thickness of the highly charged polyelectrolyte (MePVP) brush in pure water ("salt-free") is almost independent of the graft density.

Introduction

Brushes of neutral polymers and polyelectrolytes show a very interesting and rich phase behavior. In the past two decades considerable theoretical efforts have been spent on the structure of such brushes in solution. For neutral brushes, the simple scaling laws connecting molecular weight and graft density with the brush height, which were derived by Alexander[1] and de Gennes,[2,3] have largely been confirmed by more realistic mean field theories,[4−6] simulations,[7] and experiments.[8,9] The scaling results from a balance between the elastic energy and the osmotic pressure. The individual chains are entropic springs with a spring constant $\kappa = 3kT/(Na^2)$ where kT is the thermal energy, N is the chain length, and a is the segment length. The pressure exerted by the ensemble of springs P_{el} is $P_{el} = \sigma\kappa L = 3\sigma kTL/(Na^2)$, where σ is the graft density and L is the height of the brush. The osmotic pressure is given by $P_{osm} = {}^1/_2 vc^2kT$ with v the excluded volume and c the segment concentration. Setting $c = N\sigma/L$ and equating the elastic and the osmotic pressure, one arrives at the well-known scaling relation

$$L \propto N\sigma^{1/3} \tag{1}$$

For charged chains a different scaling behavior appears.[10−12] Pincus, for example, distinguishes different regimes depending on molecular mass, graft density, charge density, and ionic strength of the medium.[10] If the graft density and the charge density of "strong" polyelectrolyte brushes are high and the ionic strength is low ("salt-free" case), the brush height L_{os} scales linearly with the degree of polymerization ($L_{os} \propto N$) but is *independent* of the graft density σ. Here, the term "strong" implies that the charge on the chain is fixed. Brushes from strong polyelectrolytes are often called "quenched" brushes.

The fact that the brush thickness is independent of the graft density follows from a simple scaling consideration. If the height of the swollen polyelectrolyte brush is much larger than the electrostatic screening length, all the counterions are trapped inside the brush.[10,11] The electrostatic forces between the chains are completely screened. However, the electrostatic forces impose charge neutrality and therefore a fixed concentration of counterions. The driving force of chain stretching is the osmotic pressure of the counterions. Brushes in this regime are called "osmotic brushes". The osmotic pressure of a dilute solution of counterions is *linear* in the counterion concentration. This contrasts to polymer solutions, where the combinatorial part of the free energy is small and the excluded volume governs the osmotic pressure, resulting in *quadratic* dependence on concentration. In osmotic brushes both the elastic pressure exerted by the stretched chains and the osmotic pressure generated by the counterions depend linearly on graft density. The graft density does therefore not affect the balance between these two pressures. Thus, the brush thickness is independent of the graft density:

$$L \propto N\sigma^0 \tag{2}$$

Accordingly, neutral and charged polymer brushes fundamentally differ in their swelling behavior. Note that if very high grafting densities are considered, the excluded volume interaction can no longer be neglected in the scaling analysis of charged polymer monolayers. The osmotic brush regime would no longer apply, and the height of such polyelectrolyte brushes would become a function of the density of the surface-attached chains.[10] So far such highly grafted polyelectrolyte systems have not been realized in experimental approaches.

Schimmel et al. have previously investigated the swelling of PMMA brushes on LaSFN9 prisms.[13] The brushes were also prepared by the "grafting from" technique. It was found that the brush height increases with about the third root of the graft density. Bianco-Peled et al. have investigated the swelling of Langmuir monolayers of lipidated poly(ethylene glycol) (PEG).

† Max-Planck-Institute for Polymer Research.
‡ University of Freiburg.
§ Present address: Department of Chemical Engineering, University of California at Santa, Barbara, Santa Barbara, CA 93106.
* To whom correspondence should be addressed. e-mail: ruehe@imtek.uni-freiburg.de.

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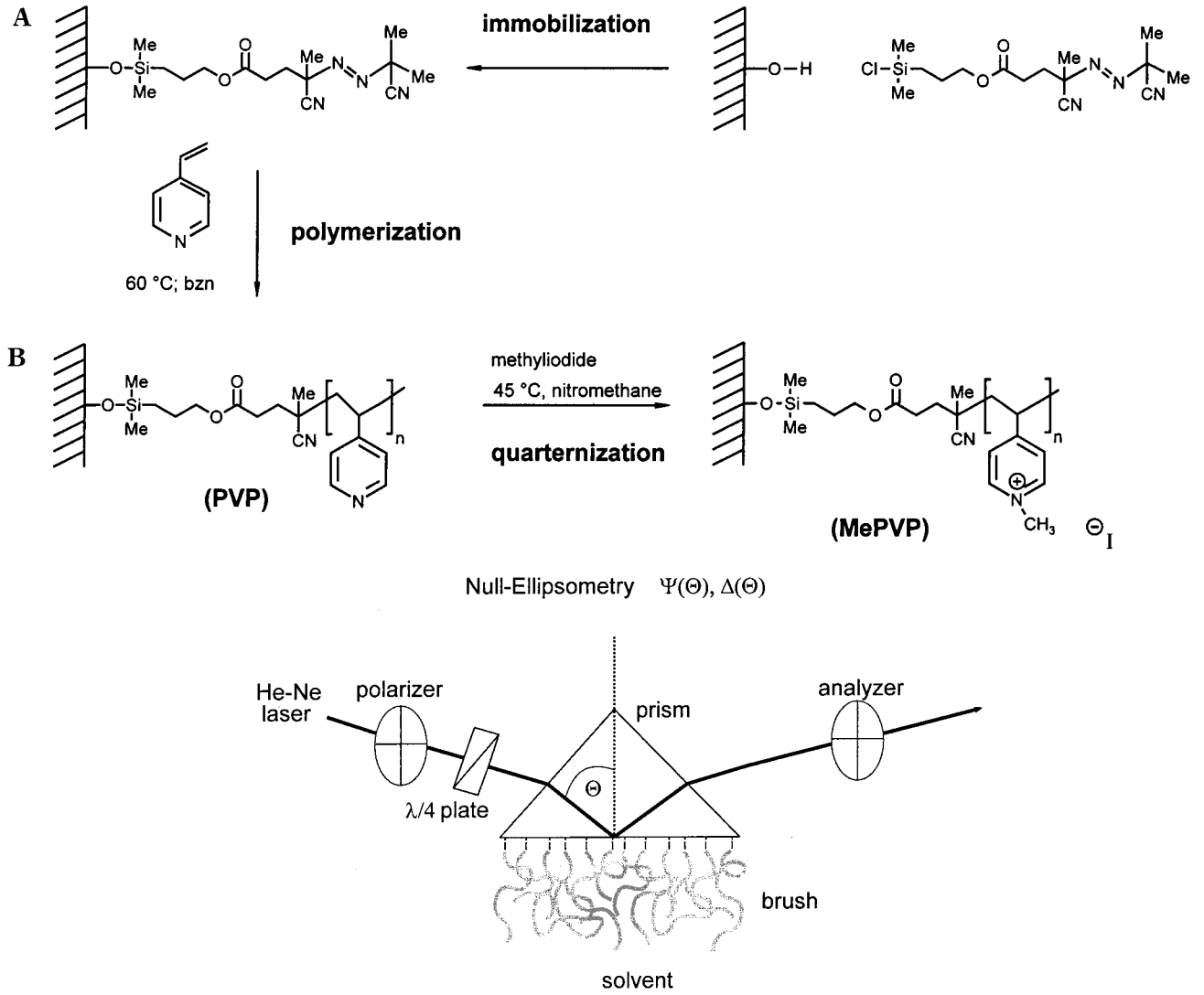

Figure 1. (A) Synthesis of a positively charged brush (poly(4-vinyl-*N*-methylpyridinium iodide)) covalently attached to a planar lanthanoxide surface. First a neutral poly(4-vinylpyridine) brush is grown by using a self-assembled monolayer of an azo initiator. The layer is subsequently converted into the polyelectrolyte brush by a polymer-analogous quaternization reaction. (B) Configuration of multiple angular internal reflection ellipsometry for the investigation of the swelling behavior of polymer and polyelectrolyte brushes.

It was found that the brush thickness in aqueous solution determined by neutron reflectometry scales as $L \propto N^{1.07}\sigma^{0.38}$.[9]

Ahrens et al. have proven the existence of an osmotic regime for a negatively charged poly(styrenesulfonate) (PSS) brush anchored at the water surface.[14,15] The anchor block of poly(ethylethylene) (PEE) formed a fluid layer at the water surface, and the PSS blocks were stretched into the aqueous solution.[14] The graft density was varied by a compression of the fluid anchor layer. X-ray reflectometry analysis showed that the brush thickness in contact with a "salt-free" aqueous solution was independent of the graft density.

Recently, we have prepared neutral polymer and polyelectrolyte brushes at a solid surface[16−18] by a "grafting from" technique.[19−22] The synthesis and the characterization of neutral poly(4-vinylpyridine) (PVP) brushes and charged (PVP quaternized with methyl iodide, MePVP) brushes are given in previous communications.[16,18] Figure 1 schematically depicts the synthesis. A PVP monolayer was grown in situ at the surface of planar glass substrates by using a monolayer of an immobilized azo initiator. The graft density and the molecular mass of the chains can be controlled by the reaction time and the monomer concentration, respectively.[19,20] The neutral PVP brush was transformed into a polyelectrolyte brush by a polymer-analogous quaternization reaction.

The thickness of neutral PVP and charged MePVP brushes as a function of the graft density of the surface-attached chains swollen in a good solvent was determined with multiple-angle null ellipsometry. These thicknesses can be compared directly to the scaling predictions. Finally, we compare the swollen heights of both the neutral and the charged polymer brushes with the contour length of the surface-attached macromolecules.

Experimental Section

Materials and Experimental Procedure. High refractive index glass prisms (LaSFN9; $n = 1.844$; Helma, Germany) were used as substrates for the deposition of the polymer layers. The prisms were activated using dilute hydrosulfuric acid (three cycles/1 min) prior to use. The immobilization of the initiator and the polymerization of 4-vinylpyridine at the surface were carried out in Schlenk tubes. Details of the procedure have been previously described.[16]

The quaternization reactions of the PVP brushes on the LaSFN9 prisms were carried out with methyl iodide (1 M in nitromethane; $T = 45$ °C; $t = 6$ h) following the procedure described by Fuoss and Strauss for the quaternization of free PVP in solution.[23] These reactions can be carried out with quantitative conversion and under mild conditions, which means that no polymer chains were cleaved from the surface.[16,18] The degree of quaternization was $f > 0.95$.[18] After completion of the quaternization reactions the samples were rinsed extensively with nitromethane to remove all of the nonreacted quaternization agents. All samples were dried in vacuum.

Instrumentation and Data Analysis. The dry and the swollen height of the brushes were determined by multiple-angle null ellipsometry. Figure 1B shows the null-ellipsometry configuration used in this study. The polymer brush is generated directly at the base side of the glass prism, and the laser light is reflected from the backside of the brush. The ellipsometric angles Ψ and Δ that correspond to the change in amplitude and phase of the light upon reflection were measured as a function of the incidence angle Θ. The setup and the data analysis have been described in detail in a separate communication.[18]

For modeling of the segment density profiles we used complementary error functions of the form

$$\varphi(z) = \frac{1}{2}\left(1 - \mathrm{erf}\left(\frac{z-d}{w}\right)\right) \qquad (3)$$

where φ is the polymer volume fraction, z is spatial coordinate normal to the surface, d is the point of inflection, and w is a measure of the smoothness of the outer edge. For box profiles the parameter w approaches zero. Complementary error functions are the simplest functions compatible with what one expects for segment density profile shapes of surface-attached polymer brushes. We do not claim that the model accurately represents the detailed shape of the profile. However, extensive testing with other model functions showed that the derived thickness, defined as twice the first moment of the profile, $d^* = 2\int z\varphi(z)\,\mathrm{d}z/\int\varphi(z)\,\mathrm{d}z$, does not depend critically on the choice of the model.

A fitting program calculates the ellipsometric spectra from the model and varies the parameters d and w to match the experimental data.[24,25] The refractive index of the pure polymer and the overall amount of polymer (known from the dry thickness) were input parameters to the calculations and kept within fixed values. An offset Δ_0 of up to 4° originating from residual stress birefringence in the prism had to be subtracted from the ellipsometric spectrum $\Delta(\Theta)$.[25] After the best fit had been determined, the thickness d^* was calculated from the first moment of the segment density profile. For a small interface width w, d^* is close to the point of inflection d. For very smooth profiles, on the other hand, d^* and d may be quite different.

A visual inspection of the data already allows for a comparison of the thicknesses under the varying conditions. This rough estimation is possible because the ellipsometric spectra below the critical angle are closely related to the Fourier transform of the segment density profile.[25] As is well-known, there is an inverse relation between the characteristic features in real space and in Fourier space. When an object increases in size in real space, its Fourier transform shifts to lower q values. This general rule applies to the ellipsometric spectra as well. The slope of $\Delta(\Theta)$ close to the critical angle is a direct measure of the brush thickness. For a low thickness $\Delta(\Theta)$ falls off rather slowly. If the brush height is large, the slope $\Delta(\Theta)$ is much steeper. This statement holds regardless of the choice of the model function used for fitting. Thus, a visual inspection of the feature close to the critical angle allows already for a rough estimation of the film thickness without any further assumptions.

Results and Discussion

Neutral PVP Brushes. PVP brushes were generated on LaSFN9 prisms with different graft densities but with a fixed molecular mass of the attached chains. Therefore, VP was polymerized in benzene solution at a fixed monomer concentration (50 mol % monomer) and a fixed temperature ($T = 60$ °C), and only the polymerization time was varied.

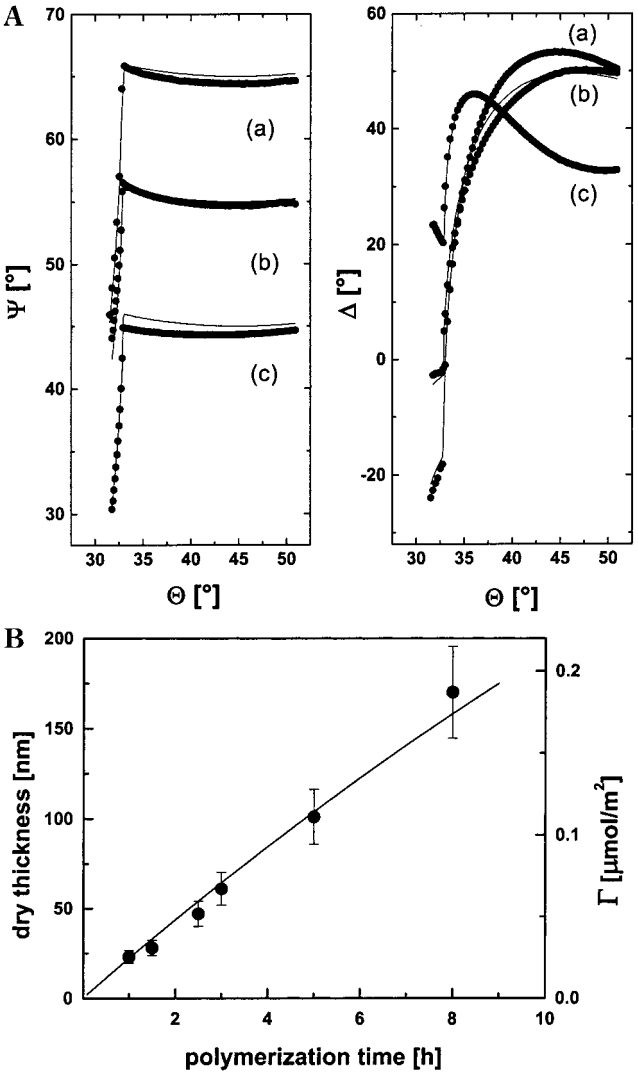

Figure 2. (A) Ellipsometric spectra (ψ and Δ as a function of the angle of internal reflection) of (a) 23, (b) 100, and (c) 170 nm (dry thickness) PVP brushes on LaSFN9 prisms in contact with air. The solid lines represent model calculations using a block profile to describe the segment density of the brushes at the surface. (B) Dry (solvent-free) thickness as a function of the polymerization time. The solid line represents the graft density calculated from the decomposition kinetics and radical efficiency of the initiator (eq 5).

The dry ("solvent-free") thicknesses of the prepared PVP brushes were determined by multiple-angle null ellipsometry. In Figure 2A ellipsometric spectra of dry PVP brushes are shown. With increasing polymerization time (resulting in an increasing graft density) (a → c) different curve shapes are obtained. We fitted the spectra with a box profile for the segment density profile. The free parameters were an offset in Δ caused by residual birefringence of the prism and the film thickness. As an input parameter, one has to give the refractive index of the polymer, which was determined separately by waveguide spectroscopy.

The fits obtained by the model calculations are shown as solid lines in Figure 2A together with the raw data of the ellipsometric measurement.

In Figure 2B the dry thickness of the PVP brush as a function of the polymerization time is shown. A dry layer thickness of almost 200 nm can be achieved within 8 h of polymerization time. The molecular mass of the surface-attached PVP chains in this case was $M_n = (1.1 \pm 0.3) \times 10^6$ g/mol, and the polydispersity was $M_w/M_n \approx 2$. Both values were determined by GPC and light scattering (SLS) for the nonattached PVP polymer formed free in solution during polymerization. As will be discussed in detail in a parallel communication,[27] the molecular mass of the free polymer is about the same as that of the surface-attached polymer chains. Typically, brushes generated by this "grafting from" technique have polydispersities of about $M_w/M_n \approx 2$ if either disproportionation or chain transfer is the terminating reaction of the surface polymerization.[19]

The number of chains per surface area (graft density) is given by

$$\sigma = \frac{\rho N_A L_{dry}}{M_n} \tag{4}$$

where L_{dry} is the dry thickness of the brush, M_n is the number-averaged molecular weight, $\rho = 1.01$ g/mol is the density of the polymer,[26] and N_A is the Avogadro constant. A frequently used parameter is the graft density Γ expressed in mol/m^2. Γ is equal to σ divided by Avogadro's number. The film growth kinetics is well described by the relation

$$\Gamma(t) = f\Gamma_0[1 - \exp(-k_z t)] \tag{5}$$

where t is the polymerization time, Γ_0 is the graft density of the initiator, f is the radical efficiency factor, and k_d is the velocity constant of the initiator decomposition. The parameters entering eq 5 have been measured for the system styrene/toluene with the same surface-attached initiator as $\Gamma_0 = 1.8$ μmol/m^2, $f = 0.4$, and $k_z = 9.6 \times 10^{-6}$ s^{-1}.[19,20] Using these parameters, we have calculated the graft density, and accordingly, with eq 4 the expected dry thickness as shown in Figure 2B (solid line). The good agreement between the measured and calculated dry thickness shows that the grafting density can be reliably and reproducibly adjusted by the polymerization time.

We now turn to the swelling behavior of the surface-attached PVP brushes under good solvent conditions. To this the PVP brushes were brought into contact with methanol and allowed to swell for approximately 0.5 h. It was observed that after this period of time no further increase of the swollen brush height occurs (data not shown here). Ellipsometric measurements were performed as described above. In Figure 3A some typical ellipsometric spectra of PVP brushes swollen in methanol are shown. It can be clearly seen that with increasing dry thickness (a → c) the curve shape changes dramatically, and a strong increase of the swollen layer thickness can be observed. Additionally, fit calculations using complementary error functions to describe the segment density profiles of the swollen layers are shown in the figure (solid lines). While at low grafting density agreement between measured and calculated curves is satisfactory, with increasing grafting density the fit calculations show significant deviations from the raw data. Especially the spectra obtained from high graft density PVP brushes can be described in a more satisfactory way if a model with a narrow interface width is used instead of the model having an exponential shape of the segment density profile (data not shown here).

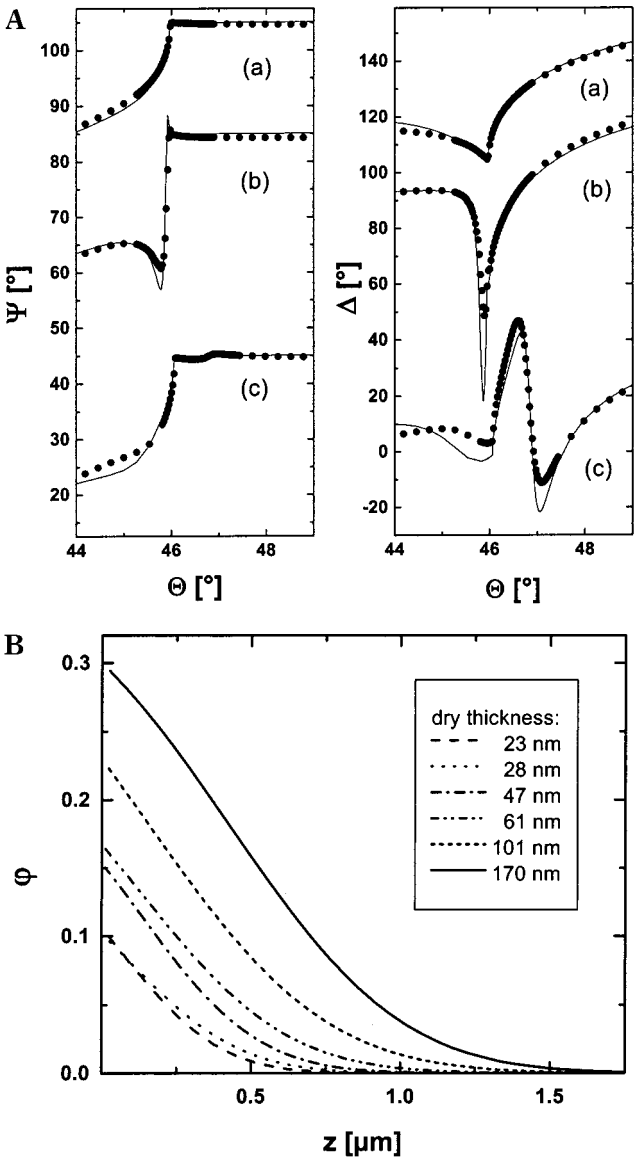

Figure 3. (A) Ellipsometric spectra (ψ and Δ as a function of the angle of internal reflection) of (a) 23, (b) 61, and (c) 170 nm (dry thickness) PVP brushes swollen in methanol. The solid lines represent model calculations using a complementary error function for the segment density profile. (B) Segment density profiles giving the best agreement with the experimental data.

In Figure 3B the segment density profiles of a PVP brush obtained from the fit calculations of the ellipsometric spectra are shown. With increasing dry thickness of the brush the chains expand further into the solution. While the dry thickness of the PVP films range on the order of 10−170 nm the swollen film thickness was determined to 300−900 nm. A satisfactory agreement between measured and calculated ellipsometric spectra is obtained if an exponential-like profile is assumed. Milner et al. theoretically investigated the influence of the polydispersity on the segment density profile of surface-attached neutral brushes.[4,5] The authors found that with increasing polydispersity of the surface-attached polymer chains the shape of the polymer segment distribution at the surface becomes exponential-

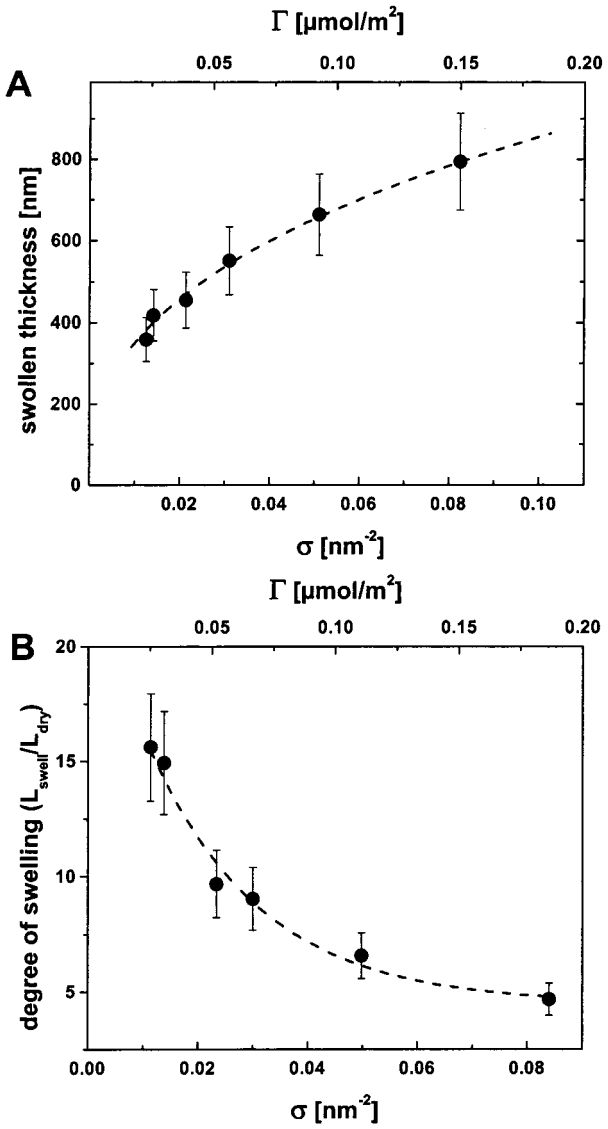

Figure 4. (A) Swollen PVP brush thickness in methanol as a function of the graft density. The thickness was calculated out of the first generalized moment of the segment density profiles. The graft density was calculated from the dry thickness of the brush, the density, and the molecular mass of the attached polymer chains. (B) Degree of swelling of the neutral brushes. The graft density was calculated from the dry thickness of the brush and the molecular mass according to eq 4. The dashed lines are guides to the eye.

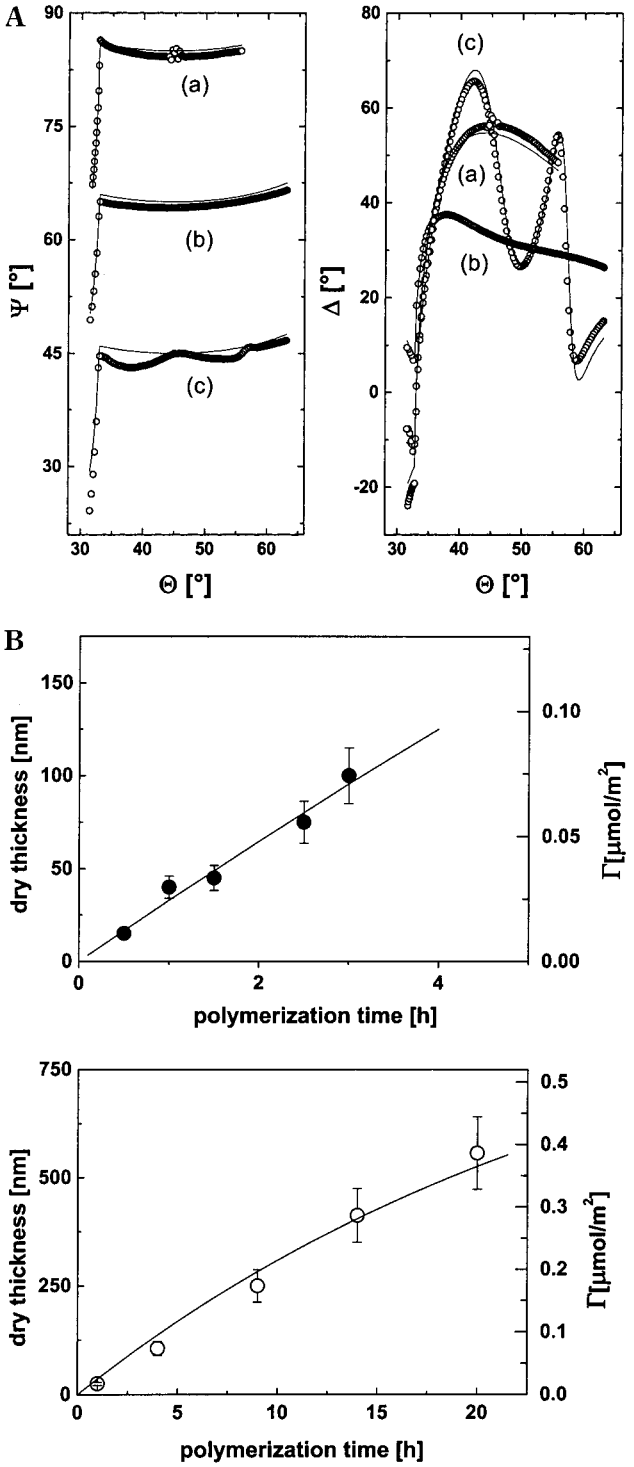

Figure 5. (A) Ellipsometric spectra (Ψ and Δ as a function of the angle of internal reflection) of (a) 40, (b) 106, and (c) 557 nm (dry thickness) MePVP brushes on LaSFN9 prisms in contact with air. The solid lines represent model calculations using a block profile to describe the segment density of the brushes at the surface. (B) Dry (solvent-free) thickness of two different polymerization series as a function of the polymerization time. The solid lines represent the graft density calculated from the decomposition kinetics and radical efficiency of the initiator.

like. These expectations agree well with the experimental data observed here.

The average swollen brush height d^* obtained from the segment density profiles is shown in Figure 4 as a function of the graft density. The graft density was obtained from the dry thickness and the molecular mass with eq 4. The best fit to our data is an exponent of 0.38 $\pm$ 0.12 indicated as a dashed line, which is only slightly higher than the $^1/_3$ predicted by theory. Although the deviation is still within the experimental error of this study, note that Schimmel and Rühe[13] and Bianco-Peled et al.[9] observed the same trend (both obtained values for the scaling exponent almost identical to the one described here).

The degree of swelling Q defined as the ratio of the swollen brush height, and the dry thickness ($Q = L_{swell}/L_{dry}$) is a direct measure for the stretching of the chains in the solvent. In Figure 4B the degree of swelling of the PVP brushes is shown as a function of the graft density of the surface-attached chains. It is evident that the degree of swelling decreases strongly with increasing graft density. For samples with high graft densities we attribute this behavior to a stretching of polymer chains even in the dry solvent-free case.

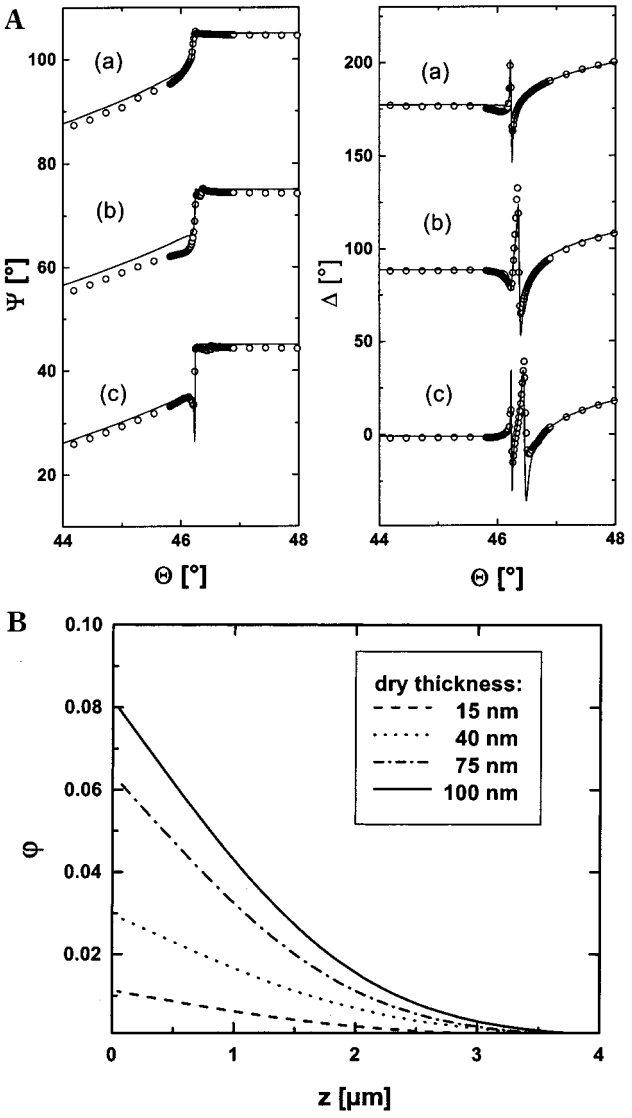

Figure 6. (A) Ellipsometric spectra (Ψ and Δ as a function of the angle of internal reflection) of (a) 15, (b) 40, and (c) 100 nm (dry thickness) MePVP brushes swollen in pure water ("salt-free"). The solid lines represent model calculations using a complementary error function for the segment density profile. (B) Segment density profiles giving the best agreement with the experimental data.

Charged MePVP Brushes. To investigate the swelling behavior of a polyelectrolyte brush in aqueous solution ("salt-free"), we have prepared MePVP brushes on LaSFN9 prisms by a polymer-analogous quaternization reaction on the prepared PVP brushes using methyl iodide as quaternization reagent. Because polyelectrolyte brushes are hydrophilic, they take up moisture depending on the relative humidity of the environment. To avoid a swelling of the MePVP layer in humid air during the measurement of the "dry" thickness of the film, a small amount of solid potassium hydroxide was placed into the sample compartment. Thereby, the relative humidity was reduced to almost 0%.[18] Figure 5A shows typical ellipsometric spectra of dry MePVP brushes. The graft density increases from part a to c. Additionally, the model fit calculations using a box model to describe the segment density of the dry polymer layers are shown as solid lines.

Figure 5B shows the dry thicknesses of the MePVP brush obtained from different polymerization series as a function of the reaction time. Both series were

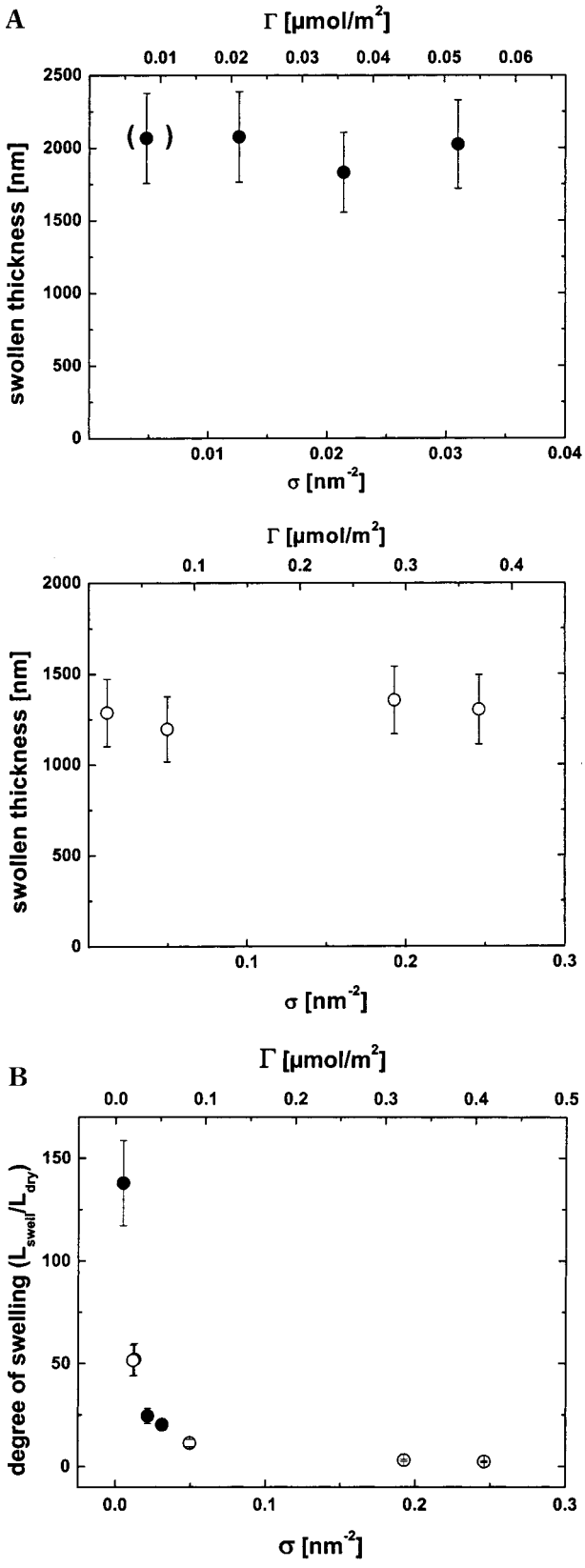

Figure 7. (A) Swollen MePVP brush thickness in pure water ("salt-free") as a function of the graft density of two different experimental brush series having different molecular masses of the surface-attached chains as described in detail in the text. The brush thickness was calculated from the first generalized moment of the segment density profiles. The graft density was calculated from the dry thickness of the brush, the density, and the molecular mass of the attached polymer chains.[28] (B) Degree of swelling of the MePVP brushes shown in (A).

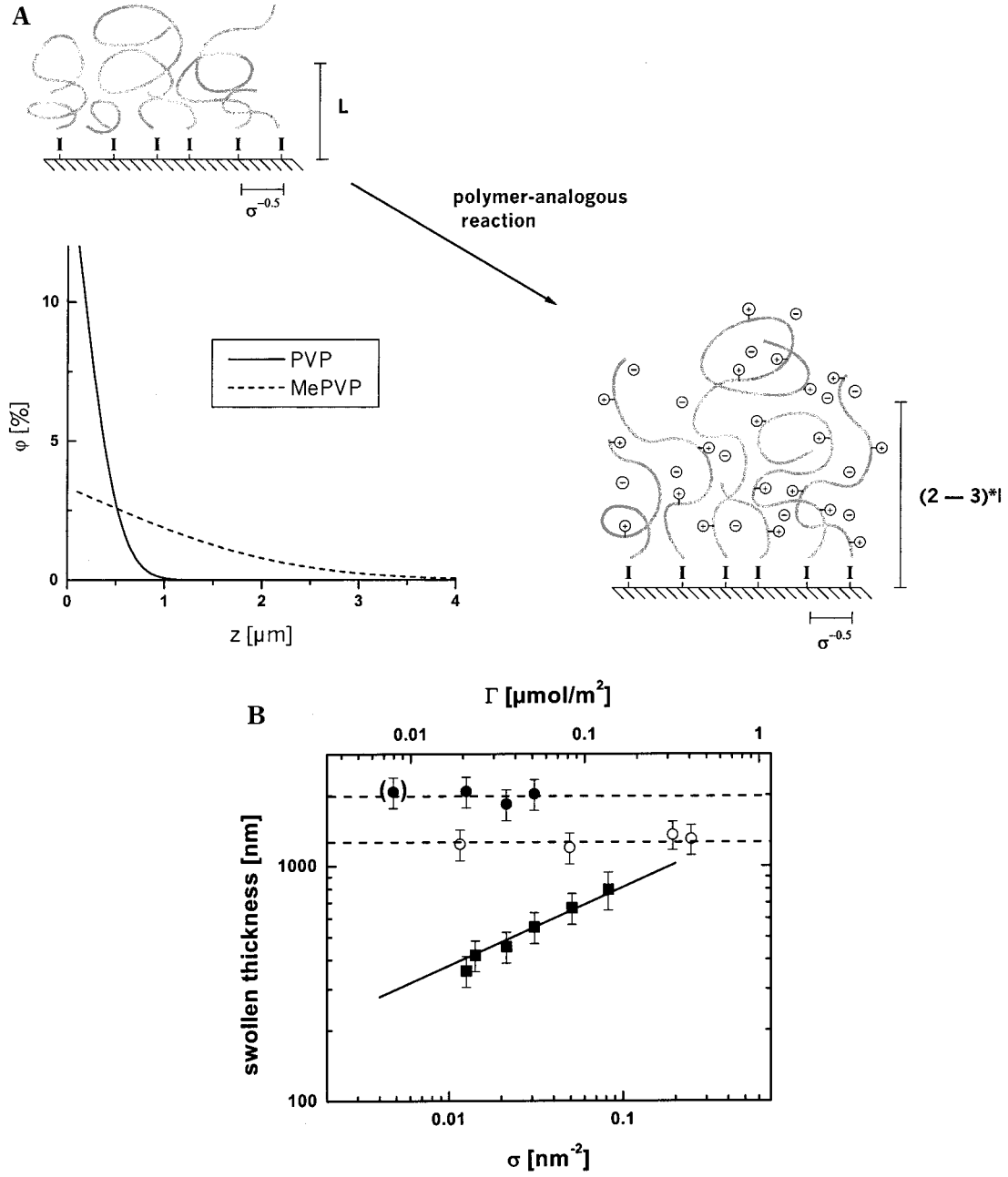

Figure 8. (A) Schematic depiction of the increase in swollen thickness of a polymer brush in a good solvent after the conversion of the neutral brush into the charged species due to the introduction of electrostatic forces. (B) Brush thickness as a function of graft density for neutral and charged brushes. The experimental results agree well with the predicted scaling laws, which are indicated as lines in the figure ($L \sim \sigma^{0.33}$ for the neutral brushes and $L \sim \sigma^{0}$ for the polyelectrolyte brushes).[28]

obtained by a polymerization of vinylpyridine in benzene solution (50 mol % monomer; $T = 60$ °C). However, it was observed that the molecular mass of the free PVP formed in solution of both series was slightly different as evidenced by GPC (series one; closed symbols in Figure 5B: M_n(PVP) = (1.1 ± 0.3) × 10^6 g/mol; series two; open symbols in Figure 5B: M_n(PVP) = (0.8 ± 0.2) × 10^6 g/mol). The solid lines in Figure 5B give the graft density and the expected dry thickness, respectively (eqs 3 and 4). The agreement of the experimental and the theoretical calculated thicknesses for both series indicate that no material is lost during the quaternization reaction.

To study the swelling behavior of the MePVP brushes, the cell was filled with pure water, and the brushes were allowed to swell for about 0.5 h. Figure 6A shows typical ellipsometric spectra of a swollen MePVP brush. The graft density increases from part a to c. In addition, calculated ellipsometric spectra are shown as solid lines. A complementary error function was chosen as a model to describe the segment density of the polyelectrolyte at the surface from which the spectra were calculated.

In Figure 6B examples for the segment density profiles of swollen MePVP brushes are shown for different dry thicknesses (graft densities) as noted in the figure. All profiles shown here were obtained from the polymerization series one (closed symbols in Figure 5B). Again, the profiles are rather exponentially shaped. Whereas in neutral brushes polydispersity increases the smoothness of the profiles,[4,5] we cannot judge the influence of polydispersity in polyelectrolytes on theoretical grounds. The experimental data suggest that the qualitative features remain unaffected. For all examples the brush height was the same at approximately 2 μm,

despite the fact that the graft density varied by a factor of 7. To study this in more detail, we have performed ellipsometric measurements on MePVP brushes with a wide range of graft densities. In Figure 7A the swollen MePVP brush height in pure water (without added salt) as a function of the graft density is shown.[28]

Here it should be mentioned explicitly that the molecular mass of the polyelectrolyte was not measured directly but calculated from the molecular mass of the PVP measured by GPC for both series, assuming quantitative conversion of the polymer-analogous quaternization reaction. The graft density was calculated from eq 4 using $\rho = 1.4$ g/mL for the density of MePVP, which was previously measured,[18] and the molecular mass of the attached MePVP chains. The molecular mass was calculated for series one (closed symbols in Figure 7A) to $M_n = 2.5 \times 10^6 \pm 0.7 \times 10^6$ g/mol and for series two (open symbols) $M_n = 1.8 \times 10^6 \pm 0.5 \times 10^6$ g/mol. Because of the differences in the molecular weight of the two series investigated here the absolute heights of both series shown in Figure 7A are different. From the experimental findings it is evident that within each series the brush height is likely to be independent of the graft density following the theoretical expectations. Part B of Figure 7 shows the degree of swelling of the MePVP brush as a function of the graft density of the surface-attached chains. Qualitatively, the same behavior as for the neutral PVP system is observed.

As the MePVP brushes are directly related to the PVP brushes from which they are synthesized, the comparison of the brush height of the neutral and the charged system allows a direct visualization of the consequence of the "switching on" of electrostatic interactions. A schematic depiction of the situation and a direct comparison of the segment density profiles for a swollen brush in the neutral state (PVP) and after addition of the charges (MePVP) is shown in Figure 8A. It should be explicitly noted that in both cases a good solvent (PVP/methanol and MePVP/water) for the respective brush was employed.

Finally, it is interesting to compare the swollen brush height of the neutral and the charged brush with the contour length of the surface-attached polymer chains. The molecular mass of the "free" PVP (series one) was measured to about $M_n \approx 1.1 \times 10^6$ g/mol. If a length per repeat unit of $a \approx 0.25$ nm is assumed, the contour length of the polymer can be calculated to roughly 2.5 μm. It is obvious that the polymer chains after conversion to the appropriate polyelectrolyte have the same degree of polymerization and therefore the same contour length. If the average swollen film thicknesses of the brushes are compared to this value, it can be concluded that the surface-attached neutral PVP chains are swollen to about 40% and the positively charged MePVP chains to more than 65% of the contour length.

Conclusions

The swelling behavior of neutral PVP as well as charged MePVP brushes with high graft densities (anchoring distance: 15 nm $< D <$ 2.5 nm) and high molecular masses ($M_n > 10^6$ g/mol) of the attached chains were studied in a good solvent by multiple-angle null ellipsometry.

Within the experimental error the swollen height of the PVP brush follows the predicted scaling law for a neutral polymer brush in a good solvent regime, where the height of the brush increases with the third root of the graft density. The height of a swollen positively charged MePVP brush in aqueous solution without added salt is in contrast to this almost independent of the graft density of the surface-attached polyelectrolyte chains. For low grafting densities of the surface-attached polyelectrolyte chains this behavior is in good agreement with predictions for an "osmotic" brush. The major difference between chemically very similar neutral and charged brushes is easily visualized if the results of the swelling studies are shown in one plot (Figure 8B). In addition, the scaling behavior ($L \propto \sigma^{1/3}$ for the neutral brush and $L \propto \sigma^0$ for the charged brush) as predicted by mean-field theory is shown in Figure 8.

In further communications we will report on the investigations of the swelling behavior of polyelectrolyte brushes as a function of the ionic strength of the environment as well as a function of the chemical charge density. Finally, in a parallel communication we are reporting on the swelling behavior of "weak" polyacid brushes as a function of the pH and external salt concentration of the solution.

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References and Notes

(1) Alexander, S. *J. Phys. (Paris)* **1977**, *28*, 977.
(2) de Gennes, P. G. *J. Phys.* (*Paris*) **1976**, *37*, 1445.
(3) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.
(4) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.
(5) (a) Milner, S. T.; Witten, T. A.; Cates, M. *Macromolecules* **1989**, *22*, 853. (b) Milner, S. T. *Science* **1991**, *251*, 905.
(6) Halperin, A. *Macromol. Rep.* **1992**, *A29*, 107.
(7) Grest, G. S.; Murat, M. In *Monte Carlo and Molecular Dynamics Simulations in Polymer Science;* Binder, K., Ed.; Clarendon Press: Oxford, 1994.
(8) (a) Klein, J. *Annu. Rev. Mater. Sci.* **1996**, *26*, 581. (b) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31.
(9) (a) Bianco-Peled, H.; Dori, Y.; Schneider, J.; Tirrell, M.; Sung, L. P.; Satija, S. *Abstr. Pap. Am. Chem. Soc.* **1998**, 364-Phys. Part 2. (b) Bianco-Peled, H.; Dori, Y.; Schneider, J.; Tirrell, M. *Langmuir* **2001**, in press.
(10) Pincus, P. *Macromolecules* **1991**, *24*, 2912.
(11) Ross, R. S.; Pincus, P. *Macromolecules* **1992**, *25*, 2177.
(12) (a) von Goeler, F.; Muthukumar, M. *Macromolecules* **1994**, *27*, 7085. (b) Misra, S.; Varanasi, S.; Varanasi, P. P. *Macromolecules* **1989**, *22*, 4173.
(13) Schimmel, M.; Rühe, J., unpublished results.
(14) Ahrens, H.; Förster, S.; Helm, C. A. *Macromolecules* **1997**, *30*, 8447.
(15) Ahrens, H.; Förster, S.; Helm, C. A. *Phys. Rev. Lett.* **1998**, *81*, 4172.
(16) Biesalski, M.; Rühe, J. *Macromolecules* **1999**, *32*, 2309.
(17) Biesalski, M.; Rühe, J. *Macromol. Symp.* **1999**, *145*, 113.
(18) Biesalski, M.; Rühe, J. *Langmuir* **2000**, *16*, 1943.
(19) Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 592.
(20) Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 602.
(21) Rühe, J. *Macromol. Symp.* **1997**, *126*, 215.
(22) Prucker, O.; Rühe, J. *Langmuir* **1998**, *14*, 6893.
(23) Fuoss, R. M.; Strauss, P. *J. Polym. Sci.* **1948**, *3*, 246.
(24) Habicht, J.; Schmidt, M.; Rühe, J.; Johannsmann, D. *Langmuir* **1999**, *15*, 2460.
(25) Biesalski, M.; Rühe, J.; Johannsmann, D. *J. Chem. Phys.* **1999**, *111*, 7920.
(26) In *Polymer Handbook;* Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989.
(27) Schimmel, M.; Rühe, J., submitted for publication.

(28) The brushes of series one were obtained directly from the neutral PVP brushes shown in Figure 4. Here the height of the MePVP brush with the lowest graft density of about $\sigma \approx 0.005$ was set in parentheses as during the quaternizatiuon reaction of this sample a significant amount of chains was lost. Therefore, a direct comparison with the PVP brush this sample was originated from is not simple. However, as under mild quarternization reaction conditions employed no chains can be fragmented, it is likely that some ester bonds that keep the polymer chains at the surface had been cleaved. Therefore, we suspect that only the graft density of the charged polyelectrolyte brush has changed compared to that of the parental PVP brush.

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