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Neutral and Charged Polymer Brushes at Solid Surfaces

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Abstract

Neutral and charged polymer brushes covalently attached to planar solid surfaces were generated by using self-assembled monolayers of an azo initiator and radical chain polymerization in situ. The brushes were characterized by FTIR-spectroscopy, optical waveguide-spectroscopy and Ellipsometry. Especially the film thicknesses of surface bound polyelectrolyte (PEL) monolayers were measured by optical waveguide spectroscopy (OWS) as a function of the humidity of the environment. The PEL brushes show strong increases in thickness as well as strong decrease of the refractive index of the surface attached layer due to water incorporation caused by the exposure to the humid environment. Aditionally the behavior of neutral as well as charged brushes in contact with solvent was investigated by using multiple-angular-scans of ellipsometry in a total internal reflectance setup. The scaling behavior of the brush height as a function of the graft density of the attached polymer molecules was investigated for the neutral brush as well as for the PEL brush system.

Introduction

The modification of solid surfaces with "tethered" polymer layers has received more and more interest in a wide field of interdisciplinary research topics ranging from areas in chemistry and physics as also in recent years in biology [1]. If the polymer chains are linked with one end to a surface and if the distance of the anchored polymer molecules is smaller than two times the radius of gyration (polymer "brush" state), the conformation of the polymer molecules at the surface is strongly different from that of "unperturbed" polymer molecules in solution. Additionally, if the surface attached layers consist of polymer molecules carry charges, structure and properties of the layers are to a large extend dominated by the electrostatic interactions.

One well known technique for the establishment of such covalently attached polymer layers is the so called "grafting to" process, where (end-)functionalized polymer molecules are covalently linked to the surface of a solid substrate. However, such a "grafting to" is generally limited in so far as only non-functionalized polymers with a rather moderate molar weight can be used for the buildup of a polymer monolayer. Furthermore the thickness of these monolay-

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ers is intrinsically limited for kinetic as well as thermodynamic reasons to thicknesses below 5 nanometer in the dry, solvent free state [2].

We report in this paper on the synthesis and the characterization of neutral as well as of charged polymer monolayers, by using self-assembled monolayers of radical chain initiators and polymerization of functional monomers at the surface of a solid substrate in situ [3]. We study the behavior of such polymer brushes in contact with different environments, by using optical-waveguide-spectroscopy as well as multiple-angular-scans of ellipsometry.

Results and Discussion

The functional polymer brushes were generated at the surface of planar glass substrates as shown in figure 1.

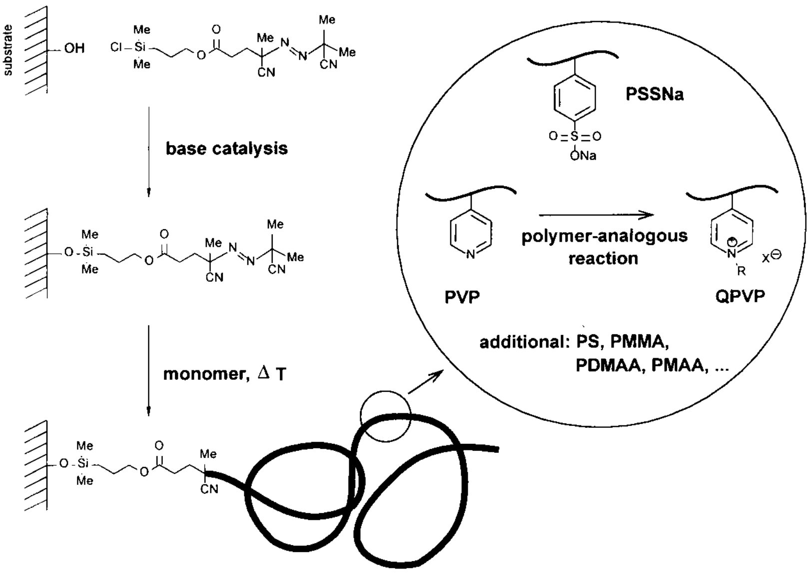

Fig.1: Preparation of polymer monolayers by using self-assembled monolayers of an azo initiator and radical chain polymerization induced by thermal energy as well as photons

The self-assembled monolayer of the azo initiators on the surface of glass-substrates were prepared via a base catalyzed condensation reaction. After this immobilization step the substrates were modified with a varity of polymer monolayers like PS, PMMA, PVP, PSSNa by thermally induced decomposition of the initiator and radical chain polymerization. For qualitative characterization of the prepared polymer brushes FTIR and additional XPS measurements were carried out. The thickness of the polymer layers were determined by using surface-plasmon-spectroscopy (SPS), optical-waveguide-spectroscopy and ellipsometry. The thickness of polymer brushes prepared by the grafting from method is a function of the molecular weight of the attached polymer chains and of the grafting density [3]. As the molecular weight of the attached chains can be controlled by choosing an appropriate monomer/solvent ratio in the polymerization step and as the graft density can be controlled by adjusting the polymerization time, films having a wide range of thicknesses starting from 2 nm up to more than 1000 nm in the dry, solvent free state can be established in a well reproducible manner. Further parameters, which influences both the graft density as well as the molecular weight are the temperature, the radical efficiency and transfer reactions.

As one example for the preparation of a neutral brush 4-vinylpyridine monomer was polymerized in benzene solution [4]. The structure of the resulting poly-4-vinylpyridine (PVP) brush was confirmed by FTIR as well as XPS measurements on the polymer layers. The thicknesses of the prepared PVP layers were determined by using optical-waveguide-spectroscopy. In figure 2 the dry (solvent free) thickness of the PVP layer is shown as a function of the polymerization time. The solid line represents the graft density of the polymer molecules calculated from the decomposition kinetics and radical efficiency of the initiator. The good agreement between the kinetics of the polymerization reaction and the measured film thickness demonstrate, that the thickness of the PVP layer can be easily controlled by adjusting the conversion of the initiator. Through a polymer analogous quarternization reaction of the pyridine moiety the neutral PVP brush can be transformed into a polyelectrolyte (PEL) brush. We have described such reactions [4,7] using different alkyl halides as quarternizing agent in nitromethane solution. The conversion of this reaction was followed by

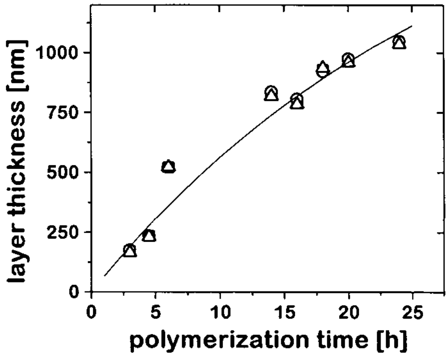

Fig.2: Thicknesses of PVP monolayers on planar glass-slide (covered with 50 nm silver and 30 nm silicon oxide) as a function of polymerization time. The thicknesses were measured by waveguide spectroscopy.

FTIR measurements. Figure 3A shows FTIR spectra of an app. 2 x 35 nm thick PVP layer measured during the quarternization using n-butyl bromide as agent in nitromethane solution after different reaction times as noted in the figure. The conversion of the reaction was calculated from the integral intensities of the absorption band due to ring vibrations of the unquarternized pyridine at 1597 cm^{-1} and from the bands of the quarternized pyridine-ring-vibrations at 1638 cm^{-1}. The conversion of the reaction as a function of the quarternization reaction time is shown in figure 3B.

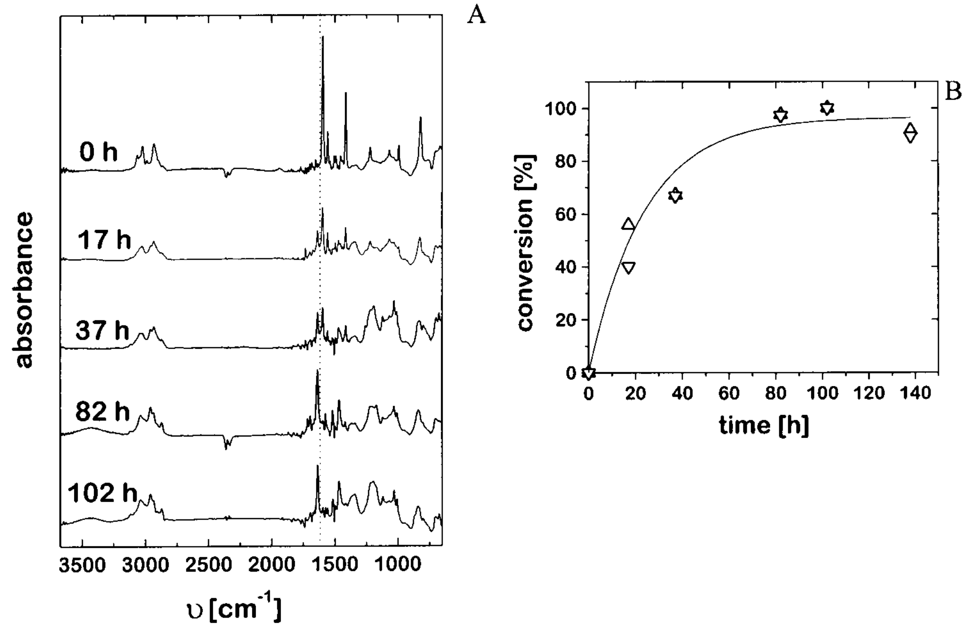

Fig.3: A: FTIR-spectra of a 2 x 35 nm thick PVP monolayer attached to both sides of a silicon-wafer. The spectra were measured during the quarternization of a covalently attached PVP monolayer at given reaction times. The quarternization was carried out with 0.5 M n-butylbromide in nitromethane at 65 °C; B: conversion of the quarternization reaction calculated by the integral intensities of the maximum of absorbance of the PVP and the quarternized PVP layer.

Additionally the kinetics of the quarternization of PVP in solution is shown in Fig. 3B (solid line) as it was measured by Fuoss and Strauss [5]. The close agreement between the conversion measured in the surface-attached monolayers and the rate of quarternization in solution clearly demonstrate that the immobilization of the chains at the surface has no significant influence on the quarternization reaction. Furthermore it is visible that the reaction can be carried out to almost quantitative conversion leading to a homogeneous distribution of the charged sites in the layer.

Additional to this two step approach for the builup of polyelectrolyte brushes at solid surfaces (generation of a neutral polymer monolayer and introduction of the charges in a second step) a poly (p-styrene-sulfonate acid) sodium salt (PSSNa) brush was synthesized in a direct procedure [6]. To achieve this the sodium salt of p-styrene sulfonate (SSNa) was polymerized in aqueous solution using the surface attached initiator as described above. In figure 4 the dry thickness of such a PSSNa brush on the surface of a silicon wafer is shown as a function of the polymerization time. It can also be seen that the thickness of the PSSNa brush can be reproducibly controlled by adjusting an appropriate polymerization time.

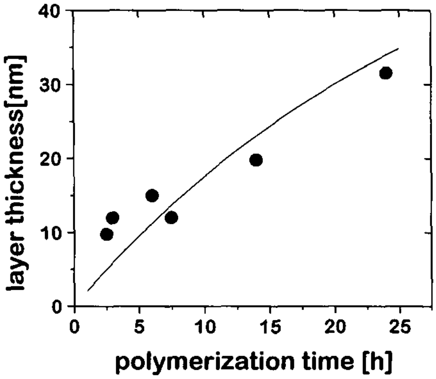

Fig.4: Thicknesses of PSSNa monolayers on silicon wafers as a function of polymerization time. The polymerizations were carried out in aqueous solution. The thicknesses were measured by null-ellipsometry.

One important property of such a PEL monolayer is its strong hydrophility. To investigate the behavior in contact with a humid environment the thickness and the refractive index of a poly-N-methyl-pyridinium-iodide (MePVP) brush was determined in environments of different relative humidity by using optical-waveguide-spectroscopy. As shown in figure 5A the sample was brought into contact with a cell, which can be held at constant temperature and at constant relative humidity. The humidity inside the cell was controlled by using small vessels filled with saturated aqueous salt solutions. The high salt content of the solution reduces the vapor pressure of the water to a highly reproducible value. During angular-scans the reflected intensity was measured as a function of the angle of incidence (Θ). By comparison of a calculated reflection curve (fresnel calculation, using a simple box model) and the experimental data, the thicknesses of the deposited polymer layer as well as the refractive index of the layer can be determined.

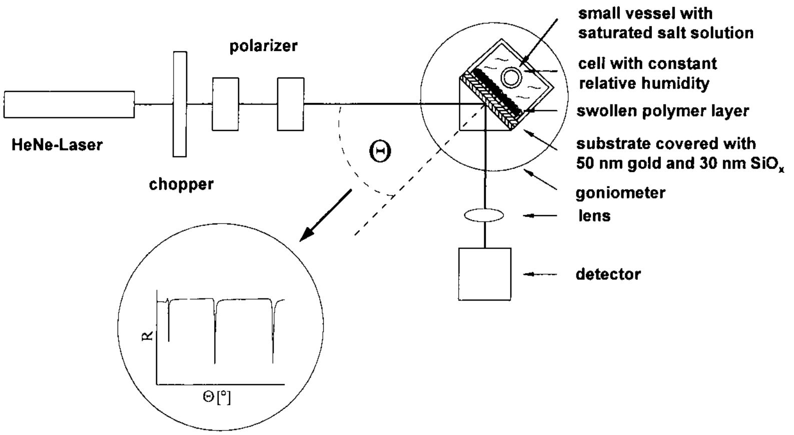

Fig.5A: Setup for waveguide-spectroscopy scan and kinetic measurements

For the determination of the thickness of the MePVP layer at a given rel. humidity the reflectivity of the sample was recorded as a function of the angle of incidence at constant temperature. The reflectivity curves are shown in figure 5B.

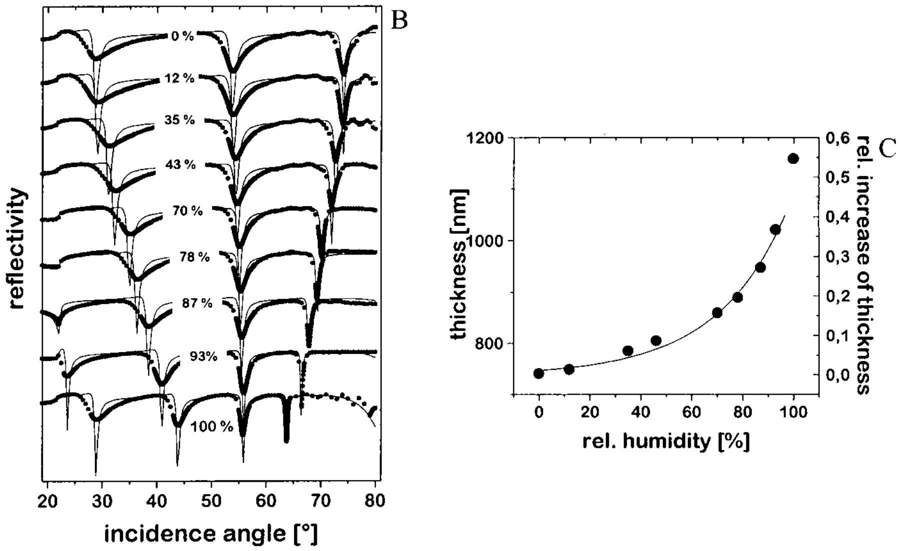

Fig.5B/C: B: Waveguide spectra (p-pol) of a 740 nm thick (dry thickness) MePVP brush on a LaSFN9/Au/SiO$_x$ substrate. The spectra were measured at different constant rel. humidities as shown in the figure. C: The thickness and the relative increase of thickness, related to the dry thickness as a function of the relative humidity of the environment. The solid line represents a guide to the eye fit.

It can be seen, that in all samples waveguide modes can be excited and that with increasing humidity of the environment the waveguide modes of higher order, which are located at lower angles of incidence, shift to higher angles. At high relative humidity even an additional waveguide mode can be observed, indicating a strong increase of thickness. The layer thicknesses as a function of the humidity of the environment are shown in figure 5C. It is evident, that with increasing rel. humidity the thickness of the polymer layer increases strongly up to values of more than 150 % of the dry thickness. The changes in film thickness due to the swelling are so very strong that they are already visible by eye through changes of the interference colors of the film. Due to the strong water uptake the refractive index of the swollen polymer film (calculated from the waveguide spectra) decreases from $n \approx 1.67$ (at 0% rel. humidity) to $n \approx 1.54$ (98% rel. humidity). Furthermore we have shown recently [7], that the swelling process is fully reversible, and that by using such thick films for the swelling in moist air differences in the rel. humidity of even less than 1 % can be determined.

Neutral polymer brushes as well as polyelectrolyte brushes show a very rich and interresting scaling behavior in contact with solvents. For the study of the brush height and the segment density profile of the surface-attached monolayers both neutral and charged polymer brushes prepared by the grafting from method were measured in solution by using multiple-angular-scans of ellipsometry in an internal reflection setup as shown in figure 6B.

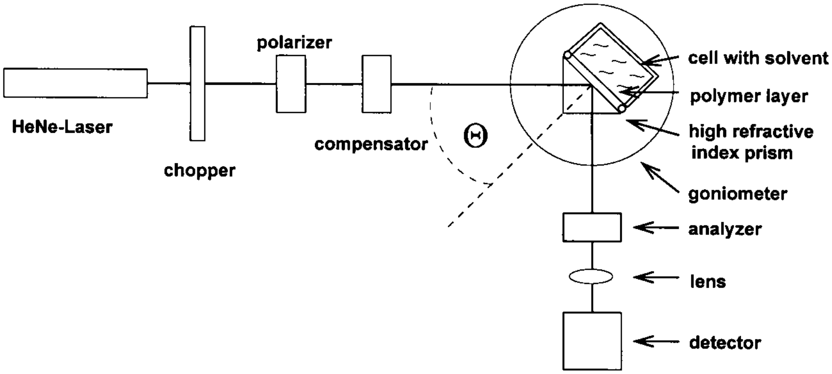

Fig.6A: Setup for multiple-angular-scans of ellipsometry in internal relectance

The ellipsometric angles Ψ and Δ were measured as a function of the reflection angle. In figure 6B such typical ellipsometry spectra of a) a bare substrate (LASFN9 prism) in contact with a solvent (in this case: methanol) and b) a app. 50 nm thick (dry solvent free thickness) PVP brush on the same prism in contact with methanol (good solvent for the PVP) are shown.

It can be seen, that the slope of the Ψ-curve close to the critical angle (noted as Θ_C in the figure) increases strongly after the deposition of the PVP monolayer, due to a considerable swelling of the PVP brush in the solvent. Also the shape of the Δ-curve changes completely. From model-fit calculations (shown additionally in the figure as solid lines) the swollen thickness and the segment density profile of the PVP layer can be calculated. Therefore we have assumed a certain profile (here: complementary error function) and have adjusted the thickness and the interface width until a good fit between calculated and measured data is obtained. In this case of the swollen PVP brush the average swollen thickness was determined to more than 1000 nm. Details of the method as well as the modell-fit calculations are described elsewhere [8].

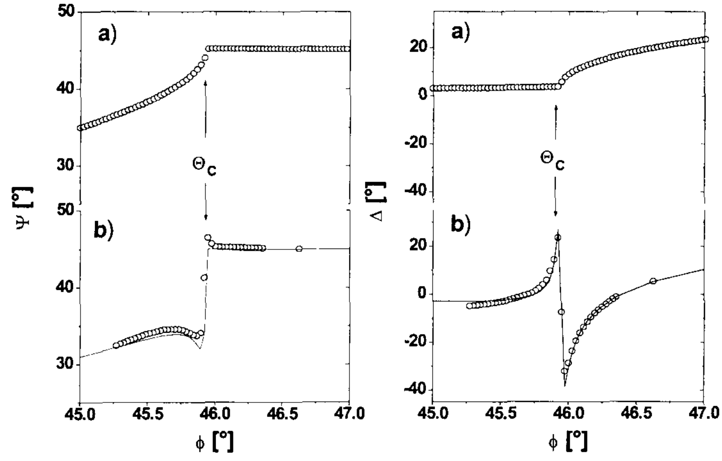

Fig.6B: Ellipsometric parameters Ψ and Δ as a function of the inner reflection angle φ of a) a pure LASFN9 prism in contact with methanol and b) a 50 nm thick (dry thickness) PVP brush on the same prism in contact with methanol. The solid lines represents the model-fit calculation using a error function as the segment profile-model of the swollen PVP brush.

We have recently studied the behavior of a PSSNa brush in aqueous solution ("salt free", millipore quality). As shown in figure 7A and 7B there are also significant changes in the ellipsometric spectra before (noted as (a) in the figure) and after (b)) modification of the substrate (LASFN9 prism) indicating a strong interaction of the layer with the solvent. The solid lines in figure 7A/B represents the model fit calculation. The segment density profile which was obtained by the model fit calculations is shown in figure 7C.

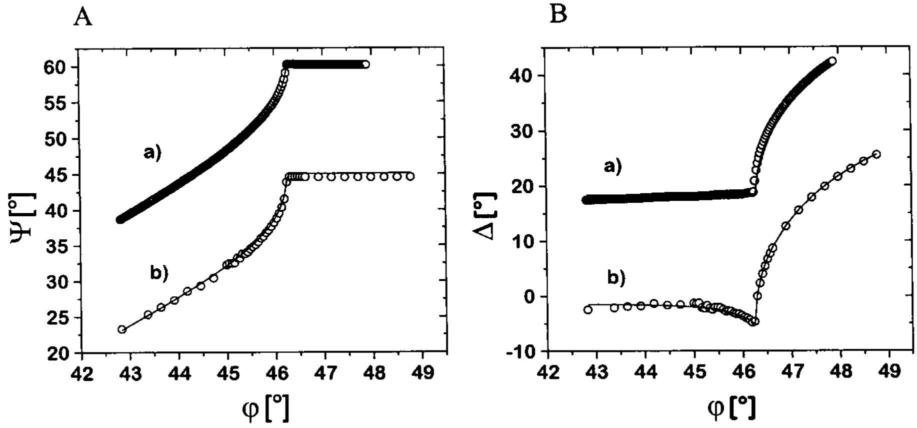

Fig.7A/B: The ellipsometric parameters Ψ (7A) and Δ (7B) as a function of the inner angle of reflection of a) a bare substrate (high refractive index LASFN9 prism) in contact with aqueous solution and b) after the deposition of a 12 nm thick (dry thickness) PSSNa brush. The solid line represents the model fit calculation using an error function.

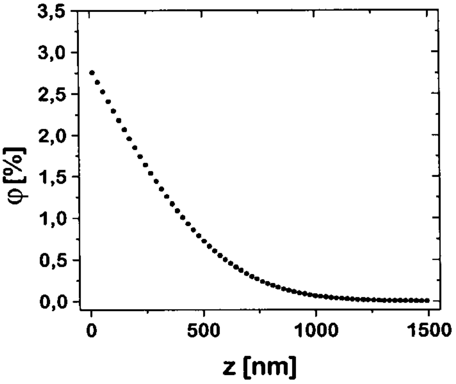

Fig.7C: Segment density profile of a 12 nm thick (dry thickness) PSSNa brush in contact with water (millipore quality). The profile was calculated from the ellipsometry measurements shown in Fig.7A/B, using an error function as a model.

It is visible that the covalently attached PSSNa layer expands strongly and diffuse into the solution. The average swollen thickness of the PSSNa brush shown in figure 7C (i.e. the first moment of the segment density profile) was calculated to 550 nm, which is in that particular case almost 60 % of the contour-length of the attached polymer chains (the contour-length was calculated from molecular weight measurements of the polymer, assuming a length of the monomer segment of l = 0,252 nm) [6].

To study the scaling behavior of a neutral brush system 4-vinylpyridine was polymerized in bulk on LASFN9 prisms at fixed temperature (60 °C), but for different polymerization times. This yields surface-attached PVP brushes which have the same molecular weight but systematically changing graft densities. The graft density of the chains was calculated from the dry, solvent-free thickness, the density of the polymer and the molecular weight of the attached chains (all parameters were seperately measured). The PVP brushes were brought into contact with methanol, which is a good solvent for PVP and multiple-angular-scans of ellipsometry were carried out. From the model fit calculations the average swollen thickness of the PVP brushes in methanol was obtained. In figure 8 the swollen thickness of the PVP brush is shown as a function of the graft density of the attached PVP chains. Additionally the theoretically predicted scaling behavior for neutral brushes is shown in the figure as a solid line.

From analytical theory as well as numerical calculations a behavior is predicted, where the brush height scales with the third root of the graft density σ of the attached chains (scaling exponent 1/3) as shown in equation 1 [9 and references therein]:

$$L_{NB} \propto \sigma^{1/3} \qquad (1)$$

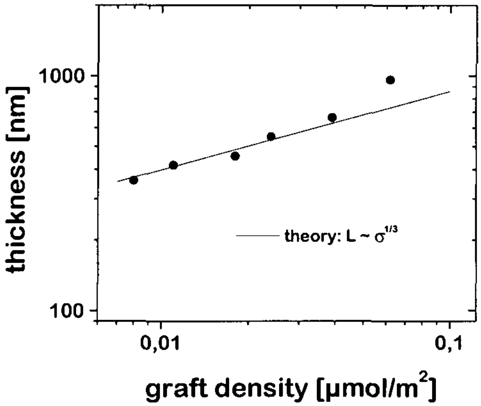

Fig.8: PVP brush thickness (swollen thickness) as a function of the graft density of the attached PVP chains. The PVP brushes were prepared on the surface of LASFN9 prisms by polymerization of 4-vinylpyridine in pure monomer at 60 °C. The swollen brush height was calculated from ellipsometric spectra.

L_{NB} is here the swollen brush height, N is the number of monomer units per chain and σ is the graft density of the attached polymer molecules. The close agreement of the experimental result and the theoretical predicted scaling behavior (Fig 8) show, that the polymer brushes obtained by the grafting from approach are suitable candidates for the investigations of the scaling behavior of surface-attached polymer monolayers. Similar results were recently obtained also for PMMA brushes prepared by the same technique [11].

The scaling behavior of charged polymer brushes differs strongly from that of uncharged brushes. As polyelectrolyte brushes consist of polyions and a tremendeous number of small counterions, the electrostatic interactions tend to stretch the brush, if brought into contact with an aqueous solution. Theoretical analysis predicts, that PEL brushes can exhibit a so called "osmotic" regime, where the swollen brush height is still a function of the molecular weight of the attached PEL chains but independent of the graft density [10].

To test the theoretical predictions we have prepared MePVP brushes, consisting of covalently bound MePVP chains with the same molecular weight but with different graft densities. The layers are essentially identical to the ones shown in figure 8 (solid signs) and from a additional series of prepared PVP brushes (open signs), however now charges were added to the polymers through carrying out a polymer analogous quarternization, using methyliodide in nitromethane solution. In figure 9 the height of such MePVP brushes swollen in pure water ("salt free") as a function of the graft density is shown.

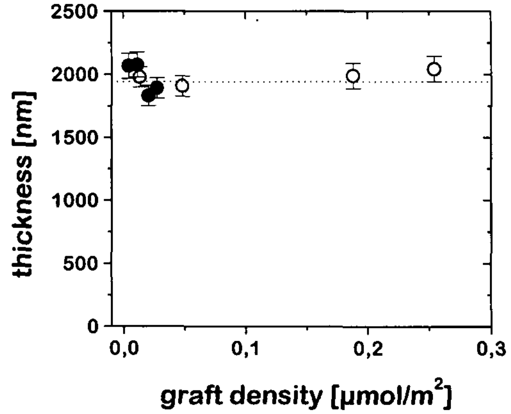

Fig.9: Swollen MePVP brush thickness in pure water as a function of the graft density of the attached MePVP chains. The MePVP brush was prepared on the surface of a LASFN9 prism via a polymer-analogous quarternizqtion reaction (methyl iodide/nitromethane; t = 6 h, T = 45 °C) on a pre-formed PVP brush. The swollen brush height was calculated from ellipsometric spectra.

It is obvious, that the scaling behavior of the charged polymer brush is completely different from that of the neutral brushes and that the swollen thickness of such a PEL brush is independent of the graft density.

Conclusions

We have shown, that by "growing" polymers from the surface of a solid substrate it is possible to synthesize charged and neutral polymer brushes. By using multiple-angular scans of null-ellipsometry and illumination from the back side of the brush it is possible to measure brush height and segment density profile of the surface-attached polymer brushes.

Acknowledgments

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References and Notes

[1] Fleer G.J, Cohen Stuart M.A., Scheutjens J.M.H.M., Cosgrove T., Vincent B., *Polymers at Interfaces*, Chapman & Hall London **1993**

[2] a) Zajac R., Chakrabati A., Phys. Rev., E; **1995**; 52, 6536 b) Kopf,A., Baschnagel, J., Wittmer, J. and Binder, K., Macromolecules, **1996**, 29, 1433

[3] a) Prucker, O. and Rühe, J., Macromolecules **1998**, 31, 592; b) Prucker, O. and Rühe, J. Macromolecules **1998**, 31, 602

[4] M. Biesalski, J. Rühe, Macromolecules **1999**, in press

[5] Fuoss R.M., Strauss P., J. Polym. Sci., **1948**, 3 (2), 246

[6] M. Biesalski, J. Rühe, submitted

[7] M. Biesalski, J. Rühe, submitted

[8] a) Habicht, J., Schmidt, M., Rühe, J., Johannsmann, D., Langmuir **1999**, 15, 2460 b) M. Biesalski, J. Rühe, D. Johannsmann, submitted

[9] a) Halperin A., Tirell M., Lodge T.P. in *Advances in Polymer Science*, 100, Springer Verlag Berlin, Heidelberg **1992** b) S.T. Milner, Science **1991**, 251, 905

[10] a) P. Pincus, Macromolecules **1991**, 24, 2912 b) F. von Goeler, M. Muthukumar, J. Chem. Phys., **1996**; 24, 11335

[10] M. Schimmel, J. Rühe, submitted