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Two Routes for Immobilization of a Hyperbranched OH-Terminated Polyester on a Silicon Surface

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Summary: Stable thin films of a hyperbranched aromatic-aliphatic OH-terminated polyester (POH) were prepared on silicon substrates. We report on grafting-to processes using macromolecular (PGMA) and bifunctional low-molecular weight coupling agents (BOX). An appropriate annealing procedure was developed for the covalent immobilization. The HBP films were characterized with spectroscopic ellipsometry, drop shape analysis (DSA), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and electrokinetic measurements. The immobilized films have an uniform surface morphology and are slightly hydrophilic ($\theta_a = 79^\circ$). The grafting process did not influence the chemical composition and the surface properties, which is important for the further application as functional layers in aqueous media.

Keywords: grafting to; hyperbranched polymers; spectroscopic ellipsometry; thin films

Introduction

The interest in hyperbranched polymers (HBP) is a result of their unique chemical and physical properties such as their globular structure, low solution viscosity and high functionality. HBPs are promising materials for biomaterial, chemical and physical applications.[1] A large amount of functional groups is available for interaction with "analyte" molecules (e.g. water, alcohols, volatile organic compounds) or biomolecules (proteins, cells). Haag et al. described the self-assembling of thin films of dendritic poly(ethylene glycol) (PEG) that hinder protein adsorption.[2] In contrast hyperbranched aromatic polyesters with hydroxyl functionalities adsorb lysozyme and human serum albumin (HSA).[3] Further applications were found, e.g. as chemical sensors.[4,5] Aromatic hyperbranched polyesters with different functionalities (hydroxyl, carboxyl, acetyl) are sensitive to alcohols and freons.[4] In previous papers we studied thin films of this polymers with regards to swelling and protein adsorption behavior.[3,6] The most investigated HBP films on solid substrates were prepared up to now by spin-coating from polymer solution without using additional coupling agents or adhesion promoters. So, only weak non-covalent interactions such as H-bonding, electrostatic or van-der-Waals forces were responsible for the substrate-layer-adhesion. Nevertheless, many applications require more stable polymer films in aqueous media. In the literature a variety of methods for the covalent immobilization of functionalized and non-functionalized polymers is mentioned. Thermoresponsive poly(N-isopropylacrylamide) (PNiPAAM)-PEG hydrogel layers have been attached by low pressure plasma treatment on thin fluorocarbon layers.[7] Stable PVME hydrogel layers were prepared by electron beam irradiation.[8] In both cases the polymers were immobilized onto the surface and partially crosslinked within the layer. Well defined polymer brushes from carboxy-terminated PS, PVP or PEG were grafted to surface modified silicon wafers.[9,10]

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Ultra thin functional films of epoxysilane (3-glycidoxypropyl-trimethoxysilane – GPS) or poly(glycidyl methacrylate) (PGMA) served as anchoring layer. The ethoxysilane and epoxy groups easily react with the activated substrate surface and form stable covalent bonds. Epoxy groups remaining after GPS or PGMA immobilization are also suitable to react with the functional groups of the top polymer and bind this polymer layer covalently. Mikhailova et al. studied the grafting of carboxy-terminated hyperbranched aromatic polyesters on thin layers of GPS.[11] A stable 12 nm thick film was formed after an annealing of 6 h at 240 °C in a vacuum oven.

Here, we present a method for covalent immobilization of an OH-terminated hyperbranched aromatic-aliphatic polyester (Figure 1) using the well-known PGMA as macromolecular anchoring layer. The reactivity of the phenolic OH groups was studied in dependence on the grafting temperature. Additionally, it was our intention to use a bifunctional coupler as crosslinker and coupling agent. Coupling reactions with bifunctional molecules such as bisoxazolines, bisoxazinones or diisocyanates are widely used in reactive blending or chain extension of polymers.[12] 1,3-Phenylenebisoxazoline was chosen in this paper. Information about the chemical composition, the thickness, the surface properties and the topography of non-grafted and grafted POH films were obtained by XPS, spectroscopic ellipsometry, electrokinetic measurements, DSA and AFM.

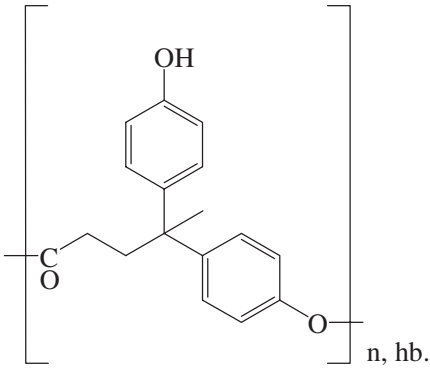

Figure 1.
Linear repeating unit of POH.

Experimental Part

Materials

The hyperbranched polyester (POH) was synthesized by melt polycondensation of 4,4-bis–(4′-hydroxyphenyl) valeric acid in an one pot reaction at 185 °C.[13] The structure and information on the chemical characterization of the polymer are summarized in Figure 1 and Table 1.

Poly(glycidyl methacrylate) (PGMA) (Mw (SEC, PS-calibration) 61 000 g/mol, PD 2) was synthesized in bulk by NMRP (T = 120 °C, time = 16 h) using glycidyl methacrylate as monomer. 1,3-Phenylenebisoxazoline (BOX) was purchased from Palmarole AG (Basel, Switzerland) and used without further purification. Ethanol, methylethylketone (MEK) and 4-methyl-2-pentanone were purchased in p.a.-grade from VWR, Merck and Fluka, respectively, and were used as received.

Substrates

Highly polished silicon wafers with a native silicon dioxide layer (~2 nm) served as substrates. The wafers were cleaned in an ultrasonic bath in dichloromethane (ACROS) for twice 5 minutes. In a second step the wafers were placed in a hydro peroxide solution (mixture of Millipore®-water, hydrogen peroxide (30%) and ammonia solution (25%), ratio of 1:1:1) for 30 min. Then the samples were carefully rinsed in Millipore®-water. The water contact angle of these silanol-rich silicon wafers pieces is near to 0°.

Film Preparation

All films were produced by spin coating in a clean room at 24 °C ± 1 °C and at a relative humidity of about 50% (Figure 2).

Table 1.
Characteristical Data of POH.

M_w [g/mol]	18 000
T_g (°C)	92
Degree of branching (Frechét)	0.5

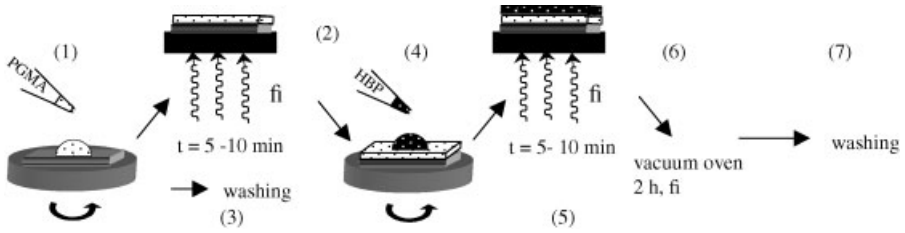

Figure 2.
Scheme of the grafting procedure (7 steps) of POH (example PGMA).

The optimal quality of the POH, PGMA or BOX layers was obtained at a rotational speed of 3000 rpm or 2000 rpm, respectively. For grafting, the PGMA or BOX layers were prepared from 0.02 wt-% solution in MEK or 0.01 wt-% solution in ethanol, respectively. In order to immobilize the spin-coated anchoring layers the samples were deposited onto a heated plate for 5 to 10 min. After the fixation the non-bound components were removed by a washing step. Then, the POH layers were applied by spin coating on top from 1 wt-% solution in 4-methyl-2-pentanone. To force the grafting-to process of the HBP layer the samples were immediately annealed on the heated plate again for 5 to 10 min. The annealing was proceeded in a vacuum oven for two more hours. The annealing of the anchoring (2) and HBP (5) layer has been carried out at the same temperature. The applied temperature range was limited by the thermal stability of BOX ($T_{annealing}$ = 150 °C–170 °C) and PGMA ($T_{annealing}$ = 110 °C–160 °C). Non-grafted polymer was removed by extraction of the films in the solvent 4-methyl-2-pentanone for 2 h. Finally, the samples were dried for 30 min at 40 °C in a vacuum oven to remove residues of the solvent.

Film Characterization

The thickness and refractive index of the POH layer were determined by a Multi Wavelength Ellipsometer M2000VI (J. A. Woollam Co., Inc.) at incident angles of 65°, 70°, 75° and wavelengths ranging from 371 nm to 1679 nm. Before, the thickness of the BOX or PGMA anchoring layers was measured at an incident angle of 70° and $\lambda = 633$ nm with a SENTECH SE-402 microfocus ellipsometer. The wetting behavior of the polymer films was investigated by advancing (θ_a) and receding (θ_r) water contact angles. Static contact angles were measured by a DSA 10 (Krüss, Germany), while dynamic contact angle measurements were performed using axisymmetric drop shape analysis (ADSA-P). The surface topography was imaged with a Dimension 3100 scanning probe microscope (Digital Instruments, Inc., Santa Barbara, CA). The chemical structure of the films was studied by XPS using an AXIS Ultra (Kratos Analytical, England). The information depth of the XPS method is not more than 10 nm in maximum. Streaming potential measurements were carried out using an Electrokinetic Analyzer EKA (Anton Paar KG, Austria).

Results and Discussion

Characterization of Non-Grafted HBP Films

The thickness of non-grafted POH films (prepared without an anchoring layer) ranges from 20 to 24 nm with a refractive index of 1.604 ± 0.007 ($\lambda = 630$ nm). AFM images of the samples revealed smooth and homogeneous films with a mean square roughness of smaller than 0.5 nm (Figure 3). In order to remove solvent traces, voids, inhomogeneities and to re-organize the polymer segments to obtain the equilibrium state of segment organization[14] the samples were annealed above T_g at 110 °C. The long-time thermal stability of the polymer

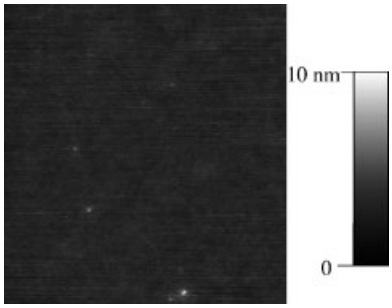

Figure 3.
AFM image of the POH film. The size is 10 μm × 10 μm.

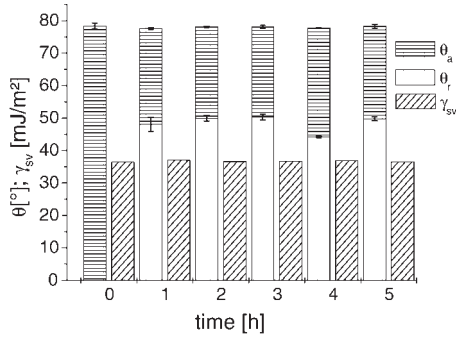

Figure 4.
Contact angles (θ) and surface free energies (γ_{sv}) of non-grafted POH films in dependence on the annealing time (T = 110 °C).

was separately studied by thermogravimetric analysis. The analysis of the XPS C 1 s spectrum showed that about 5% of all carbon atoms of the outer polymer surface layer are connected to hydroxyl groups (corresponds to theoretical values). Hence, a largely hydrophilic surface was expected. The results of the water contact angle measurements are shown in Figure 4. An advancing contact angle of ~79° indicates only slightly hydrophilic surfaces (cp. PS $\theta_a = 90°$). However, we assume that the aromatic rings influence the surface properties strongly. It can be clearly seen, that the annealing process does not remarkably change neither the contact angle values nor the surface free energy. Storing at room temperature seems to be adequate for reorganization of hydrogen bonds and polymer segments after spin coating since the aliphatic backbone part of the polymer is quite flexible. This can be seen in the lower T_g compared to a fully aromatic structure ($T_g = 227$ °C).[11]

Characterization of Grafted POH Films

1. PGMA Anchoring Layer

The synthetic procedure was started with the grafting of the PGMA layer to the silicon wafer (Figure 5). The annealing supports the formation of covalent bonds due to the reaction of epoxy groups and Si-OH groups. On the surface of the PGMA about one third of the functional groups are remaining epoxy groups (XPS). The PGMA layer thickness was determined with 1.5 nm ± 0.1 nm (refractive index fixed at n = 1.525).[15] AFM-measurements confirmed uniform covering of the surface (Figure 6a). In a second step the HBP layer was deposited on the PGMA layer according to Figure 2. The additional annealing step (5) on the heated plate is necessary to obtain a remarkable reaction between the largely inert phenolic OH groups of the HBP and the epoxy groups of the PGMA. Films, which were only annealed in the vacuum oven (5), were characterized by

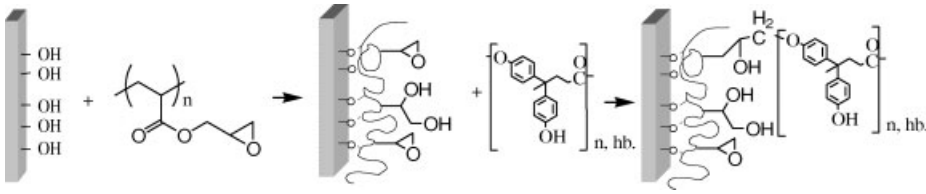

Figure 5.
Scheme of the grafting of POH on PGMA anchoring layer.

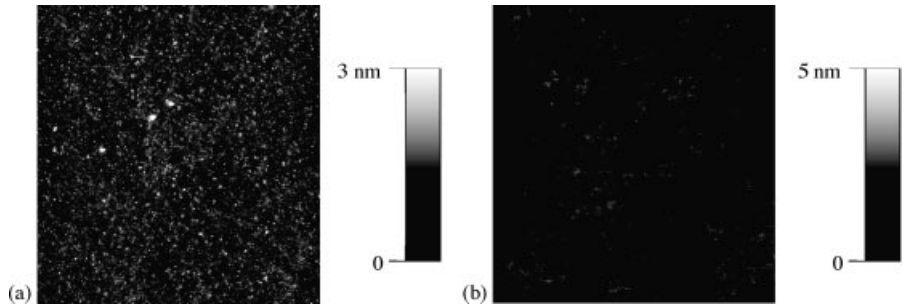

Figure 6.
AFM-height-image: (a) PGMA layer; (b) HBP grafted on PGMA. The size is 10 μm × 10 μm.

lower refractive indexes. This indicates a reduced grafting density. Only with an optimized grafting-procedure it was possible to obtain immobilized polymer layers of hydroxyl-terminated HBP on silicon substrates modulated in thickness.

Obviously, high temperatures and a direct supply of thermal energy are necessary to promote the reaction and reduce the dwell time. The attachment of HBP was studied in dependence on the annealing temperature varied from 110 °C to 160 °C. Annealing at 110 °C led to films with low grafting degree indicated by a low mean effective refractive index (Figure 7). However, increasing the temperature at 120 °C and above the amount of covalently grafted HBP is strongly increased. Figure 7 shows that the appropriate grafting temperature is 160 °C. Under this conditions it is possible to produce dense and homogeneous HBP films (Figure 6b). The refractive index after extraction n equals the refractive index of the non-extracted polymer film n_0. Surprisingly the thickness remained nearly constant clearly indicating that not only monolayers of the POH were prepared ($t_{monolayer} \leq 5$ nm).

Thicker films were grafted from solutions with concentrations between 2 wt-% and 4 wt-%. After extraction films with a HBP layer thickness up to 70 nm could be determined. That means, this synthetic concept is also suitable for the preparation of defined layers with a considerably larger thickness (Figure 8). The lower HBP layers are covalently immobilized by its reaction with the PGMA's epoxy-groups. The rather short chains of the PGMA are not able to penetrate through a 70 nm thick polymer

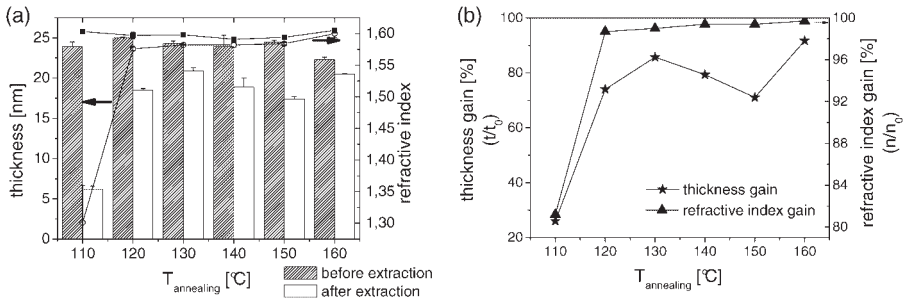

Figure 7.
(a) Temperature-dependent grafting; (b) Increase of thickness gain t/t_o ★ (t_o – thickness after immobilization, t – thickness after extraction) and increase of the refractive index gain n/n_o ▲ (n_o – refractive index after immobilization, n – refractive index after extraction) with temperature.

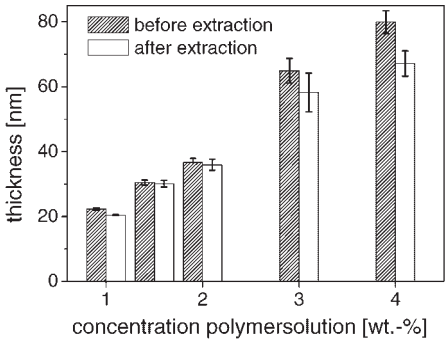

Figure 8.
Concentration-dependent thickness of the grafted layers.

layer and cannot fix the upper HBP layers. Sidorenko et al. investigated the self-assembling of aliphatic hyperbranched polyesters (core: 2-ethyl-2-(hydroxymethyl)-1,3-propandiol (TMP)) from acetone solution.[16] After a simple washing step bilayers of the polymers (thickness approx. 3 nm) were formed by weak hydrogen bonds. Our investigations showed that the hydrogen bond network widely influences the film properties.[17] This hydrogen-bond network has at least a strong influence on the immobilization. Intermolecular ether formation induced by the annealing might be another reason of further stabilization. This will be the topic of another paper.

It is important to note that the grafting process should not affect surface properties, especially the availability of the functional groups. Different methods for the characterization of the grafted layers were carried out. In order to separate the OH groups the polymer film was labeled with trifluoroacetic anhydride. In presence of OH groups the anhydride forms a fluorinated ester. The fluorine signal can be detected in the XPS spectra and from its intensity the number of accessible and reactive OH groups can be estimated. The recorded spectra showed that the number of surface OH groups remained constant. Hence, no changes in the surface wettability parameters were observed and the number of protonable groups, expressed by the isoelectric point (IEP), which was determined from the streaming potential experiments do not show significant changes (Table 2). The refractive index of the grafted and extracted samples is very similar to the values obtained for non-grafted polymer films.

2. Use of bifunctional coupler

In a second approach 1,3-phenylene-bisoxazoline (BOX) was used as anchoring layer. In Figure 9 the supposed POH surface reaction on the BOX modified Si-wafer is illustrated. The mean effective

Table 2.
Comparison of characteristic data of the non-grafted and grafted HBP.

Sample	IEP	θ_a[°]	Thickness [nm]	n ($\lambda = 630$ nm)
PGMA		72.8 ± 1.2	1.5 ± 0.1	1.525 (fixed)
grafted, after extraction	4.1	79.4 ± 0.5	20.5 ± 0.1	1.600 ± 0.006
non-grafted	3.8	78.1 ± 0.2	21.9 ± 0.8	1.604 ± 0.007

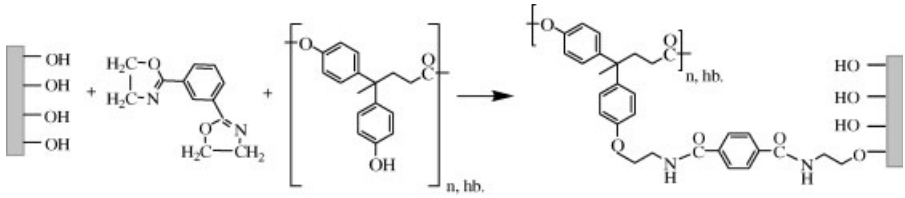

Figure 9.
Reaction of BOX and POH in a thin film.

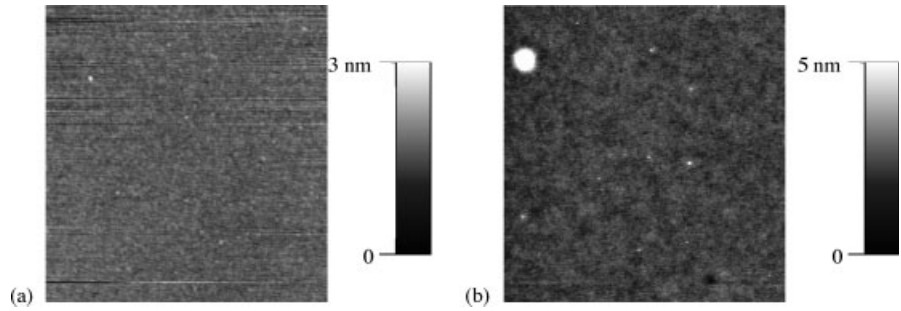

Figure 10.
AFM-height image: (a) BOX-layer; The size is 2 μm × 2 μm. (b) grafted POH layer ($T_{grafting} = 170\ ^{\circ}C$). The size is 10 μm × 10 μm. The white spot is a dust particle.

thickness of the primary BOX layer (confirmed by XPS) was determined by mapping ellipsometry to be approx. 0.3 nm.

AFM measurements confirmed smooth and uniform BOX layers with a mean square roughness of <0.2 nm (Figure 10a). We applied the thermal grafting procedure described above for the POH immobilization on PGMA (Figure 2). Here, the annealing temperature ranged from 150 °C to 170 °C. After extraction the films were characterized by ellipsometry (Figure 11, Table 3) and AFM (Figure 10b). As mentioned above the increase of the annealing temperature results in an increase of the thickness of the grafted layer. Two hours of annealing at 170 °C were appropriate for the POH immobilization on the bisoxazoline anchoring layer. The POH films were smooth and homogeneous with a mean square roughness smaller than 0.6 nm (Figure 10b). The values of the water contact angles and the refractive indexes equals the values obtained for non-grafted polyester films (Table 4). The XPS-spectra were comparable to the spectra of the non-grafted films.

The comparison of the two couplers shows that ultra thin PGMA layers allow the immobilization of thicker POH films than BOX using the same grafting conditions. This is caused by the different amount of reactive sites, which are available on the surface of the anchoring layers. Significantly more functional groups are located in the ''loops'' and ''tails'' of one anchored PGMA chain[18] compared to only one oxazoline group which serves as reactive site in the BOX molecules. Also both oxazoline groups of one molecule can react with the substrate and then are no longer available for attachment of the HBP.

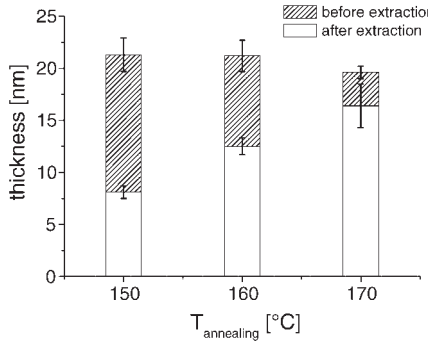

Figure 11.
Temperature dependent grafting.

Conclusion

We have investigated the properties of thin aromatic-aliphatic hyperbranched OH-terminated polyester films. We fabricated

Table 3.
Comparison of the refractive index after immobilization and extraction in dependence on the temperature.

Sample	Refractive index ($\lambda = 630$ nm)	
	Immobilization	Extraction
160	1.604	1.578
170	1.598	1.592

Table 4.
Comparison of characteristic data of a non-grafted and differently BOX grafted HBP (after annealing at three temperatures and subsequent extraction).

Sample	θ_a[°]	θ_r[°]	Thickness [nm]	n ($\lambda = 630$ nm)
150 °C	79.5 ± 0.9	37.9 ± 0.2	8.1 ± 0.6	1.600 (fixed)
160 °C	80.3 ± 1.0	43.8 ± 1.0	12.5 ± 0.8	1.578 ± 0.012
170 °C	81.7 ± 0.7	41.9 ± 1.2	16.4 ± 2.1	1.592 ± 0.006
Non-grafted HBP	78.1 ± 0.2	50.0 ± 0.9	21.9 ± 0.8	1.604 ± 0.007

homogeneous and molecularly smooth films and characterized them regarding their surface properties, chemical composition and optical constants. Furthermore, we found methods to immobilize the OH-terminated polyester on an activated silicon substrate in short time using different anchoring layers. PGMA and for the first time a bifunctional coupling agent – BOX – were used as reactive ultra thin anchoring layers. The thermal grafting was only successful if a controlled heating/annealing procedure could be realized. The wetting properties and the morphology of the resulting stable HBP layer were not influenced by the grafting procedure.

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[1] C. Gao, *Prog. Polymer. Sci.* **2004**, *29*, 183–275.
[2] C. Siegers, M. Biesalski, R. Haag, *Chem. Eur. J.* **2004**, *10*, 2831–2838.
[3] Y. Mikhailova, V. Dutschk, M. Müller, K.-J. Eichhorn, B. Voit, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2007**, *297*, 19–29.
[4] G. Belge, D. Beyerlein, C. Betsch, K.-J. Eichhorn, G. Gauglitz, K. Grundke, B. Voit, *J. Anal. Bioanal. Chem.* **2002**, *274*, 403.
[5] M. Vollprecht, F. Dieterle, S. Busche, G. Gauglitz, K.-J. Eichhorn, B. Voit, *Anal. Chem.* **2005**, *77*, 5542–5550.
[6] Y. Mikhailova, V. Dutschk, C. Bellmann, K. Grundke, K.-J. Eichhorn, B. Voit, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2006**, *279*, 20–27.
[7] D. Schmaljohann, J. Oswald, B. Jorgensen, M. Nitschke, D. Beyerlein, C. Werner, *Biomacromolecules* **2003**, *4*, 1733–1739.
[8] J. Hegewald, T. Schmidt, U. Gohs, M. Günther, R. Reichelt, B. Stiller, K.-F. Arndt, *Langmuir* **2005**, *21*, 6073–6080.
[9] S. Minko, S. Patil, V. Datsyuk, F. Simon, K.-J. Eichhorn, M. Motornov, D. Usov, I. Tokarev, M. Stamm, *Langmuir* **2002**, *18*, 289–296.
[10] K. S. Iyer, B. Zdyrko, H. Malz, J. Pionteck, I. Luzinov, *Macromolecules* **2003**, *36*, 6519–6526.
[11] Y. Mikhailova, E. Pigorsch, K. Grundke, K.-J. Eichhorn, B. Voit, *Macromol. Symp.* **2004**, *210*, 271–280.
[12] L. Jakisch, H. Komber, R. Wursche, F. Böhme, *J. Appl. Polym. Sci.* **2004**, *94*, 2170–2177.
[13] R. Weberskirch, R. Hettich, O. Nuyken, D. Schmaljohann, B. Voit, *Macromol. Chem. Phys.* **1999**, *200*, 863–873.
[14] Y. Tang, J. R. Lu, A. L. Lewis, T. A. Vick, P. W. Stratford, *Macromolecules* **2002**, *35*, 3955–3964.
[15] D. W. Van Krevelen, "*Properties of polymers*", Elsevier, Amsterdam **1997**, p. 82.
[16] A. Sidorenko, X. W. Zhai, S. Peleshanko, A. Greco, V. V. Shevchenko, V. V. Tsukruk, *Langmuir* **2001**, *17*, 5924–5934.
[17] Y. Mikhailova, G. Adam, L. Häussler, K.-J. Eichhorn, B. Voit, *J. Mol. Struct.* **2005**, *788*, 80–88.
[18] B. Zdyrko, V. Klep, I. Luzinov, *Langmuir* **2003**, *19*, 10179–10187.

