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Surface Properties and Swelling Behaviour of Hyperbranched Polyester Films in Aqueous Media

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Summary: Thin films of hydroxyl (POH) and carboxyl (PCOOH) terminated aromatic hyperbranched polyesters (HBPs) were prepared by spin coating on silicon wafers and subsequently annealed above their glass transition temperature (T_g). The surface properties and the swelling behaviour of these films in aqueous buffer solutions were studied as a function of annealing time using contact angle measurements and ellipsometry. Non-annealed films were hydrophilic with surface free energies of 51 mJ/m^2 for POH and 49 mJ/m^2 for PCOOH, respectively. The swelling behaviour of the polymer films in buffer solution with pH 7.4 was described in terms of changes of the thickness and effective refractive index of the swollen layer. Under identical conditions a lower water uptake was found for hydroxyl terminated HBPs (POH) which were annealed more then 2 h. The lower water uptake correlates with the surface properties of the films. The annealed films were less hydrophilic. Their surface free energy was 38 mJ/m^2 independent of the annealing. Films of carboxyl terminated HBPs (PCOOH) showed similar surface properties after annealing. However, these films were unstable under the same conditions in aqueous solutions. Stable PCOOH films were obtained by additional covalent binding to the substrate using an epoxy silane as a coupling agent.

Keywords: grafting to; hyperbranched polymers; surface free energy; swelling behaviour

Introduction

The increased attention to thin films of HBP on solid substrates is connected with their potentially interesting properties as chemical sensors, diagnostic tools and functional coatings due to their high number of functional groups in a highly branched architecture. [1,2] In a previous paper[3], we studied the surface properties of thin films of hyperbranched aromatic polyesters terminated with hydroxyl and carboxyl groups and found that these polymers had hydrophilic surfaces caused by acidic functional groups at the outermost surface. Using spectroscopic ellipsometry and reflectometric interference spectroscopy, the swelling behaviour of the HBP films was studied at different atmospheric humidity. From the results, it could be concluded that HBP films can be used potentially as sensoric materials. In this work, we are interested in the

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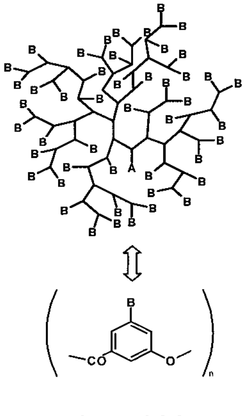
application of HBP films as biofunctional materials. Since the media in which biomolecules, such as proteins, usually interact are aqueous solutions, we studied the behaviour of HBP films in buffer solutions (pH=7.4) and used hyperbranched aromatic polyesters having hydroxyl and carboxyl end groups.

The films were characterized with regard to their chemical composition, thickness, optical constants and morphology using FTIR, NMR, ESCA, ellipsometry methods and scanning force microscopy. Their surface properties were determined by contact angle and zeta potential measurements. The swelling behavior of the films in contact with electrolyte solutions was investigated in situ by spectroscopic ellipsometry.

Experimental section

Materials. Hydroxyl (POH) and carboxyl (PCOOH) terminated hyperbranched polyesters with the same backbone structure were synthesized by Schmaljohann[4] using melt polycondensation of AB_2 monomers. Before the investigations the polymers were purified and structures were checked by NMR and FTIR measurements. The information concerning structure and properties are shown in Figure 1 and Table 1.



B = OH or COOH

Figure 1. Schematic structure of HBPs

Table 1. Chemical characterisation of HBP

material	M_w [g/mol]	T_g [°C]	$T_{annealing}$ [°C]	branching degree
POH	16.000	227	240	0.60
PCOOH	15.500	214	240	n.d.

n.d. – not determined

Substrates. The substrates were polished silicon wafers with native (~ 2 nm, for Null-ellipsometry) and thermally oxidized (~ 55 nm, for spectroscopic ellipsometry) silicon dioxide layers. For cleaning of the silicon wafers dichloromethane of 99.5% purity (Acros) in an ultrasonic bath (2 times for 5 min) and a hydroperoxide bath (a mixture of water, ammonia solution (25%) and hydrogen peroxide (30%) in volume ratio 1:1:1) at 60 °C for 1 hour were used. Then the samples were washed with the reagent–grade water produced by Milli-Q filtration system and dried with argon. Using the hydroperoxide bath, it was possible to transform the surface (Si-O-Si) of the natural SiO_2 layer into a surface dominated by Si-OH groups without destruction of the surface.

Preparation of the non–grafted polymer layers. A 1 wt% solution of HBP in distilled tetrahydrofuran (THF, Merck) was used for spin coating. Annealing of HBP films above T_g leads to removing of voids and inhomogeneities in the polymer layer due to release of stress within the films and better segregation between fragments.[5] The resulting roughness (rms roughness value) of all polymer films was in the range of 2 nm (determined by AFM for a scan size of 20x20 μm^2).

Preparation of the grafted polymer layers. The grafted PCOOH layers were prepared via a "grafting to" approach using 3-glycidoxy-propyltrimethoxy silane (GPS)[6,7] as coupling agent (Figure 2). For the chemisorption the GPS was used as 1 wt% solution in dry toluene and contacted with the wafer surface for 16 h in a special box with an argon atmosphere. Then the wafers were washed two times in dry toluene in the argon box and three times in ethanol for removing non-grafted GPS. Afterward the wafers were dried under argon stream. The thickness of the GPS layer obtained by Null-ellipsometry was in the range of 0.6 nm. PCOOH were prepared by dip coating from 2 wt% solution in THF. Then the samples were annealed above T_g at 240 °C in vacuum oven (Transparent Drying Oven Buchi model T0-51) for 6 h. The non-grafted polymer was removed by a THF soxhlet extraction for 4 h.

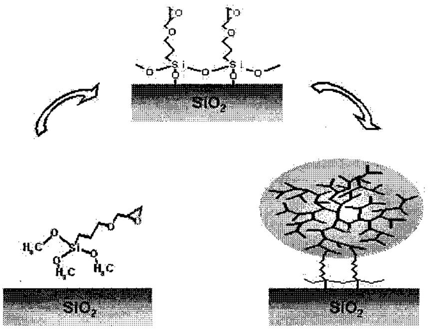


Figure 2. Grafting of PCOOH to the silicon substrate

Sample Characterisation

Ellipsometry. The thickness and optical constants of the HBP films were measured by a multiwavelength ellipsometer M-44 (VASE, J.A. Woollam Co., Inc). The samples were positioned in the central area of a quartz cell and held by a special Teflon holder. The light beam was directed to the middle of the sample surface at an incidence angle of 68 °C. The ellipsometry measurement was started with determination of the thickness and refractive index of the dry film in air at 22°C and 40-50% relative humidity. Then buffer solution (phosphate buffer, pH 7.4, Aldrich) was introduced in to the cell and subsequent time dependent ellipsometry autoscans were started.

The different steps of PCOOH grafting were characterized by Null-ellipsometry (SE402, Sentech) with a He–Ne laser (λ = 633 nm) and an angle of incidence 70°. The layer thickness values were calculated using the corresponding refractive indices of the polymers determined by spectroscopic ellipsometry and Cauchy layer optical models (Table 2).

Table 2. Refractive indices (n) and extinction coefficients (k) used for thickness calculations (λ = 630 nm)

material	Si[1]	SiO_2[1]	GPS[2]	POH[2]	PCOOH[2]
n	3.875	1.4571	1.4290	1.6500	1.6170
k	0.016	0	0	0	0

where [1] and [2] – optical constants are taken from literature and determined by spectroscopic ellipsometr, respectively.

The swelling degree (SD) of the layers was defined by following equation:

$$SD\,(\%) = [(D_\infty - D_0)\,/\,D_0]\ x\ 100 \qquad (1)$$

where D_∞ and D_0 are the equilibrium thickness values of the HBP film in swollen and dry state, respectively.

Contact angle measurements. Surface wettability and hydrophilicity of HBP films on smooth silicon wafers were investigated by advancing and receding contact angle measurements (DSA-

10 Krüss, Hamburg, Germany) using fresh ultrapure water (MilliQ, Millipore) in laboratory atmosphere. Each reported contact angle measurement represents an average value of 2 or 3 separate drops on different areas. The solid surface tension (γ_{SV}) was calculated by combining the Young equation:

$$\gamma_{LV}\cos\Theta = \gamma_{SV} - \gamma_{SL} \tag{2}$$

and the equation of state for solid-liquid interfacial tensions:[8]

$$\gamma_{SL} = \gamma_{LV} + \gamma_{SV} - 2\sqrt{\gamma_{LV}\cdot\gamma_{SV}}\cdot e^{-\beta(\gamma_{LV}-\gamma_{SV})^2} \tag{3}$$

where γ_{LV} and γ_{SL} are the liquid–vapour and solid–liquid interfacial tension, respectively. β is an empirical constant (0.0001247). Combining eq. (2) and eq. (3) one yields the following relation:

$$\cos\Theta = -1 + 2\sqrt{\frac{\gamma_{SV}}{\gamma_{LV}}}e^{-\beta(\gamma_{LV}-\gamma_{SV})^2} \tag{4}$$

According to eq. (4) the solid surface tension γ_{SV} can be calculated from the experimentally measured contact angle (Θ) and the known γ_{LV} of water (72.5 mN/m).

For the investigation of the contact angles as function of time the dynamic measurements of the Axisymmetric Drop Shape Analysis – profile (ADSA) was used.[9,10] The same samples were used as for the ellipsometric measurement.

Results and Discussion

Swelling measurements of POH

The initial measurements of the dry film gave a thickness in the range from 34 to 37 nm with the refractive index of 1.650 at λ = 630 nm (Figure 3). These values were taken as starting points for the following measurements. Time-dependent data of the thickness of POH layers in the buffer solution were obtained using a simple optical model (Si/SiO_2/swollen polymer/water)[11]. Figure 3 clearly shows the strong effect of the film annealing on the swelling behaviour of POH films. An increase of the annealing time correlates with a decrease of swelling. This behaviour can be a result from a combined effect of the improved structural reorganization of hydrophobic and hydrophilic segments press towards to become better segregated within the film [5,12]. The swelling kinetics can be described by a two steps mechanism: During the first step 90 % of water is sorbed in the film within seconds. This can be classified by Fickian diffusion law. Water molecules penetrate into microvoids and free volume of the HPB and interact via hydrogen bonds. As result of the corresponding out-of-plane expansion a thickness increase is observed. At the same time the uptake of the "optical thinner" water (n=1.33) gives a decrease of the effective refractive index of the swollen layer. The second, much slower, step is due to relaxation process within the layer. The changes in conformation of the polymer molecules allow the layer to absorb the additional water molecules.

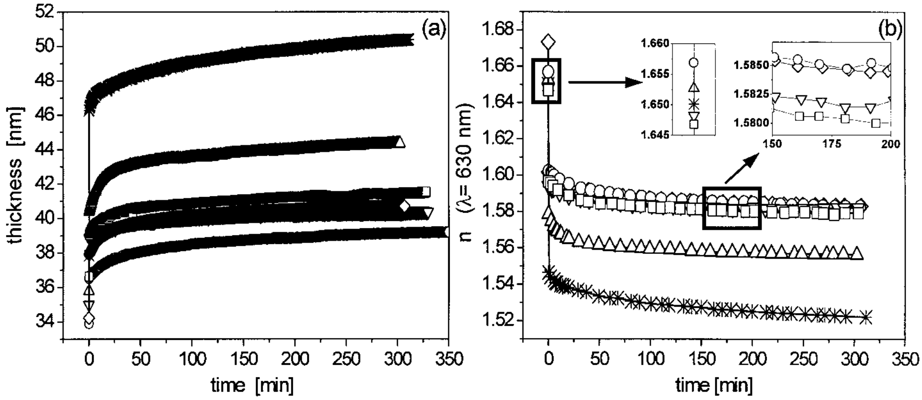


Figure 3. Changes of thickness (a) and refractive index (b) of POH films annealed for different times: 0h (*), 1h (Δ), 2h (◊), 3h (o), 4h (∇), 5h (□)

The refractive indices for the swollen films of POH annealed from 3 till 5 hours are similar and are around 1.58. The swelling degrees at different annealing time are shown in Figure 4. The similar swelling degrees of polymers annealed from 3 to 5 hour demonstrate that a time of 3 h is enough for full segment reorganisation within the polymer film.

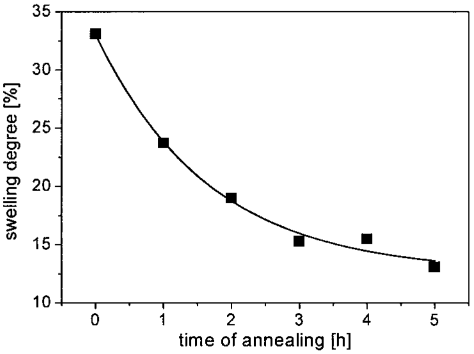


Figure 4. Equilibrium swelling degree of POH films as a function of annealing time

To prove the reversibility of the swelling process, the POH films were removed - from buffer solutions after experiment, washed with water, dried under an argon stream and stored under constant conditions for three days.[10] Then the measurement of the polymer layer thickness was repeated. It gave a thickness having a variation of about 4 % from initial state. Hence, a completely reversible swelling process occurs.

The results of the water contact angle measurements for POH films with different time of annealing are presented in Table 3. It can be clearly seen, that changes in the surface-energetic properties occurred after 1 hour of annealing and that after longer annealing time further changes did not take place. The non-annealed surface has a surface free energy of 51 mJ/m^2 while the annealed surfaces yield surface free energies of about 38 mJ/m^2 independent of the annealing time.

Table 3. Effect of annealing time on advancing and receding contact angles and solid–liquid surface tension of POH surface

time of annealing [h]	advancing contact angle (Θ_a) [deg]	receding contact angle (Θ_r) [deg]	$\Delta\Theta = \Theta_a - \Theta_r$ [deg]	γ_{sv} [mN/m]
0	54.0 ± 0.4	20.1 ±1.3	55.1	51.2
1	75.2 ± 0.8	34.6 ±1.3	40.6	38.3
2	75.1 ±1.0	36.4 ± 1.2	38.7	38.3
3	75.8 ±0.6	33.7 ±1.4	42.1	37.9
4	75.6 ± 0.9	35.1 ± 0.6	40.5	38.0
5	76.6 ± 1.4	37.9 ± 1.3	38.7	37.4

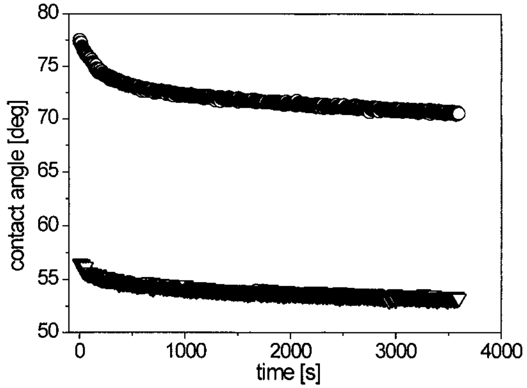


Figure 5. Time-dependent contact angle measurements of water on annealed (○) an non-annealed (▽) POH films using ADSA

If a water droplet is placed on the POH film and the time-dependence of the contact angle is measured by ADSA a small decrease of the water contact angle is observed after a few minutes on both, the non-annealed and the annealed POH surface (Figure 5). These changes in the water contact angle can be related to the swelling of the film.

Grafting reaction and surface characterisation of PCOOH

The contact angles and surface free energies of simply spin-coated, non–attached PCOOH layers as a function of the annealing time are shown in Table 4.

Table 4. Results of the contact angle measurement for spin-coated, non-grafted PCOOH annealed at different times

time of annealing [h]	advancing contact angle (Θ_a) [deg]	receding contact angle (Θ_r) [deg]	$\Delta\Theta = \Theta_a - \Theta_r$ [deg]	γ_{sv} [mN/m]
0	57.7 ± 1.6	19.6 ±1.0	38.1	48.6
2	69.9 ± 0.3	25.3 ±0.4	44.6	41.2
4	73.8 ± 1.5	28.4 ±0.1	45.4	38.8
6	73.8 ± 1.1	29.4 ± 0.3	44.4	38.8

Different annealing times were used to find the optimal conditions for preparation of the polymer films. The surface-energetic properties of the PCOOH films were changed similarly to the POH films by annealing: The originally hydrophilic PCOOH surface was changed into a surface with a lower surface free energy. After an annealing time of 4 h, no further change in the surface properties was observed. In the case of PCOOH, it is assumed that intermolecular and intramolecular reactions between carboxylic groups of PCOOH occur during annealing. As a result anhydride groups could be formed in dependence on temperature and humidity. It is known from contact angle measurements on dry hydrolyzed (i.e. exhibiting carboxylic groups) and annealed (i.e. having anhydride surface groups) polymer films that anhydride groups are less hydrophilic.[13]

Figure 6 shows the “dissolution behaviour” of PCOOH/GPS reactive layers after different times of annealing to initiate the thermal grafting process. The initial film thickness on the GPS modified wafer after spin-coating was ~ 35 nm. The films with 2 and 4 hours of annealing disappeared from the surface of the wafer. The six hours annealed film was not removed from the substrate. It swells strongly, as expected, up to 55 nm.

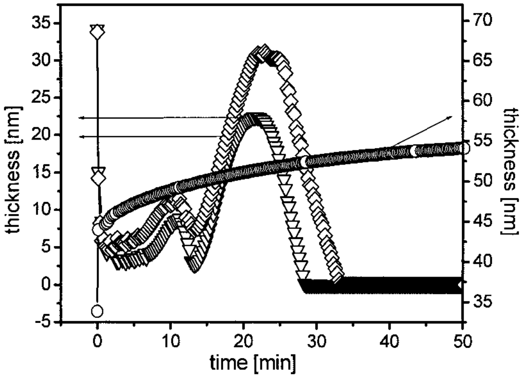


Figure 8. Time dependent swelling of non-extracted PCOOH/GPS samples with different times of annealing to proceed the grafting reaction: 2 h (▽), 4 h (◇) and 6 h (○)

These results show that non-attached PCOOH layers are not stable under the used conditions (pH ≥7). Therefore, it is necessary to form PCOOH layers which are covalently bound to the substrate. The surface properties of the GPS and PCOOH grafted layers after extraction are presented in Table 5. The advancing contact angle of the grafted PCOOH layer was found in the range between contact angles of non-annealed and 2h annealed non-grafted PCOOH (Tab.4).

Table 5. Results of the contact angle measurements on GPS and grafted PCOOH (non-grafted polymer was removed by soxhlet extraction)

material	Thickness [nm]	advancing contact angle (Θ_a) [deg]	receding contact angle (Θ_r) [deg]	$\Delta\Theta = \Theta_a - \Theta_r$ [deg]	γ_{sv} [mN/m]
GPS	0.6	47.1 ± 1.3	29.2 ± 3.0	17.9	55.5
graft–PCOOH	12.0	63.7 ± 1.5	17.7 ± 1.3	46.0	45.4

Conclusions

In summary, we have investigated the surface properties and the swelling behaviour of different annealed HBPs. It was shown that the stability of non–covalently attached HBP layers in aqueous solutions was strongly dependent on the type of functional groups. Stable films of PCOOH were obtained only by covalent grafting onto the modified substrate. POH layers swell clearly, reversibly and with similar kinetics (very fast initial phase, then reaching a plateau), and a corresponding change in thickness and refractive index was measured. The swelling behaviour strongly depends on: initial layer thickness, type of functional groups, buffer type, annealing procedure. The lower water uptake of the annealed films correlated with the less hydrophilic surface properties. Therefore, for the application of HBP films as biofunctional materials, a control of the swollen HBP layer is necessary if subsequent protein adsorption experiments will be carried out which are in the scope of our interest at present.

Acknowledgment

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(1) B. Voit, *J. Polym. Sci. Part A: Polym. Chem* **2000**, *38*, 2506.
(2) G. Belge, D. Beyerlein, C. Betsch, K.-J. Eichhorn, G. Gauglitz, K. Grundke, B. Voit, *J. Anal. Bioanal. Chem.* **2002**. *374*. 403.
(3) D. Beyerlein, G. Belge, K.-J. Eichhorn, G. Gauglitz, K. Grundke, B. Voit, *Macromol. Symp.* **2001**,*164*, 117.
(4) D. Schmaljohann "Funktionalisierung von hochverzweigten Polyestern für den Einsatz als Beschichtungs- und Blendmaterial" Herbert Utz Verlag, Wissesnchaft, München **1998**
(5) Y.Tang, J.R. Lu, A.L. Lewis, T.A. Vick, P.W. Stratford, *Macromolecules*, **2001**, *34*, 8768.
(6) S. Minko, S. Patil, V. Datsyuk, F. Simon, K.-J. Eichhorn, M. Motornov, D. Usov, I. Tokarev, M. Stamm, *Langmuir* **2002**, *18*, 289.
(7) A. Sidorenko, X.W. Zhai, A. Greco, V.V. Tsukruk, *Langmuir* **2002**, *18*, 3408.
(8) D.Y. Kwok, A.W. Neumann, *Adv. Colloid Interface Sci.* **1999**, *81*, 167.
(9) D.Y. Kwok, T. Gietzelt, K. Grundke, H.-J. Jacobasch, A.W. Neumann, *Langmuir* **1997**, *13*, 2880.
(10) K. Grundke, C. Werner, K. Pöschel, H.-J. Jacobasch, *Colloids and Surfaces Part A* **1999**, *156*, 19.
(11) R. F. Peez; D. L. Dermody; J. G. Franchina; S. J. Jones; M. L. Bruening; D. E. Bergbreiter; R. M. Crooks, *Langmuir* **1998**, *14*, 4232.
(12) Y. Tang, J.R. Lu, A.L. Lewis, T.A. Vick, P.W. Stratford, *Macromolecules*, **2002**, *35*, 3955.
(13) P. Uhlmann, S. Skorupa, C. Werner, K. Grundke, submitted for publication in Langmuir.