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ORIGINAL CONTRIBUTION

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Tailored modification of quartz surfaces by covalent immobilization of small molecules (γ-aminopropyltriethoxysilane), monodisperse macromolecules (dendrimers), and poly(styrene/acrolein/divinylbenzene) microspheres with narrow diameter distribution

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Abstract Quartz plates were modified by consecutive immobilization of γ-aminopropyltriethoxysilane (APTS), phosphorus containing dendrimers with aldehyde groups (generation 5 – G5), Starburst PAMAM dendrimers generation 4 (G4-PAMAM), and poly(styrene/acrolein/divinylbenzene) microspheres [P(SAD)]. In this way surfaces with heterogeneity on molecular, macromolecular, and microscopic levels, and which were equipped with functional amino or aldehyde groups were obtained. Surface layers were characterized by X-ray photoelectron spectroscopy (XPS) and by contact-angle measurements. Analysis of XPS spectra revealed that the thickness of the layer of G5 on the SiO_2-APTS substrate was 3.7 nm, i.e., the thickness was typical for macromolecular dimensions. The average thickness of the layer of PAMAM dendrimers on SiO_2-APTS-G5 was found to be 0.35 and 0.29 nm, depending on whether calculations were based on attenuation of the intensity of the Si2*p* or the P2*p* signal respectively. This thickness was unreasonably low for a monolayer of PAMAM dendrimers and indicated that the surface of the SiO_2-APTS-G5 substrate was incompletely covered with these macromolecules. The XPS method was also used for the determination of the degree of coverage of the surface of a SiO_2-APTS-G5-PAMAM plate with P(SAD) microspheres. The degree of coverage was found to be 0.60 and approaches the maximum theoretically possible value (0.62) for microspheres attached chaotically and irreversibly to the surface in an arrangement one microsphere thick. Subsequent coverage of the SiO_2-APTS-G5-PAMAM-P(SAD) substrate with PAMAM dendrimers resulted in the formation of a PAMAM adlayer 3.2 nm thick, close to the molecular dimensions of these dendrimers. Contact-angle measurements revealed considerable differences in the hydrophobicity of the surfaces of the quartz plates, depending on their modification. Hydrophobicity increased in the order SiO_2 < SiO_2-APTS-G5-PAMAM < SiO_2-APTS ≤ SiO_2-APTS-G5 < SiO_2-APTS-G5-PAMAM-P(SAD).

Key words Quartz – Dendrimers – Microspheres – X-ray photoelectron spectroscopy – Wettability

Introduction

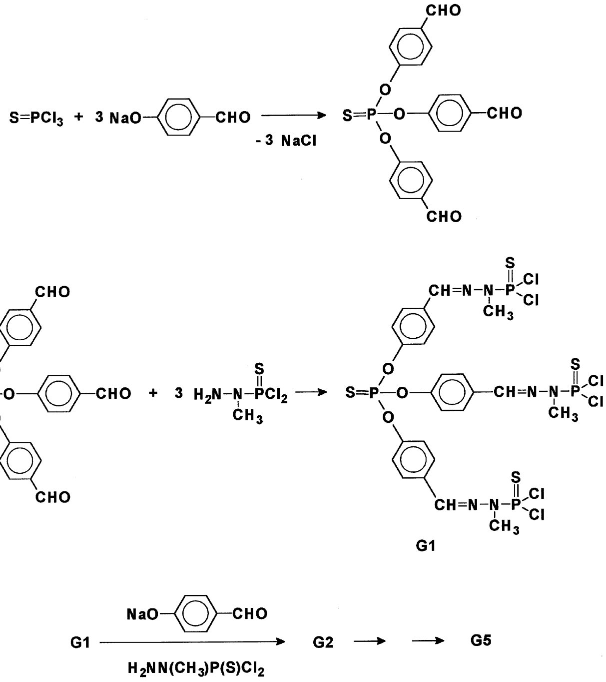
Materials with tailored surface properties are used for various important applications, in particular for adsorption and/or covalent immobilization of catalysts, enzymes, other proteins suitable for medical, veterinary, and environmental analysis, as well as for immobilization of living cells [1–13]. In many instances it is not only desirable to produce plates, powders, and other products with the required reactive groups at their surfaces but also to control the surface roughness on the molecular and supramolecular level. Surfaces of quartz, various glasses, and silica were modified by covalent immobilization of silanes [14–17], by adsorption and chemical grafting of macromolecules of synthetic and natural polymers [18–21], and by attachment of latex particles [8, 22–25]. Recently there were reports on modification of quartz, glass, and silicon by covalent immobilization of dendrimers [26, 27].

Our efforts are directed toward development of new and better materials suitable for application in the construction of biosensors and other devices used in medical diagnostics. In many instances it is necessary to immobilize bioactive compounds (e.g., proteins) onto surfaces of elements of biosensors (often made of quartz, glass, silicon, and/or gold) in a tailored way, via molecular and/or macromolecular spacers. Therefore, we wanted to develop methods suitable for the sequential coverage of quartz with layers of γ-aminopropyltriethoxysilane (APTS), monodisperse macromolecules–dendrimers with CHO and NH_2 reactive groups, and microspheres with CHO groups [poly(styrene/acrolein/divinylbenzene) particles] [P(SAD)]. In this way we hoped to obtain modifying layers with thickness varying from a few angstroms (modification with APTS) to nanometers (by immobilization of dendrimers), and eventually to hundreds of nanometers (modification by binding microspheres). One important question we wanted to answer was whether deposition of the above-mentioned modifying agents results in formation of monolayers or in the multilayer attachment of each of them with a thickness difficult to control. We were also interested in attachment of human serum albumin (HSA) onto these surfaces. HSA was chosen for our studies as a protein most abundant in blood and in some other body fluids. Therefore, immobilization of HSA (model protein) onto surfaces of materials considered as candidates for construction of biosensors is of primary importance. To characterize the modified quartz plates we used X-ray photoelectron spectroscopy (XPS) and contact-angle measurements.

Experimental

Materials

Very pure quartz (fused silica, Carl Zeiss, Jena) was used to make slides. According to the supplier, the quartz contained Al (0.05 ppm), Na (0.1 ppm), Ca (0.4 ppm), Ti (0.08 ppm), Fe (0.1 ppm), Cu (0.05 ppm), Cr (0.01 ppm), Mn (0.01 ppm), and Pb (0.02 ppm) in addition to SiO_2. APTS (Aldrich) was used without further purification. Dendrimers with CHO groups, generation 5 (G5), were synthesized as described by one of us earlier [28–30] according to the following scheme. In addition to carbon, hydrogen, and oxygen these dendrimers also contained phosphorus, nitrogen, and sulfur atoms.



Dendrimers with NH_2 groups (Starburst PAMAM, generation 4, 10% w/w in methanol, Aldrich) (denoted in the following as PAMAM) were used as received. The chemical structure of PAMAM dendrimers is as follows: $[\text{-}CH_2N[CH_2CH_2CONHCH_2CH_2N[CH_2CH_2CONHCH_2CH_2N[CH_2CH_2CONHCH_2CH_2N[CH_2CH_2CONHCH_2CH_2N(CH_2CH_2CONHCH_2CH_2NH_2)_2]_2]_2]_2]_2$. P(SAD) microspheres with CHO groups were synthesized and purified as described earlier [31]. Microspheres were characterized by the following parameters: number average diameter $\bar{D}_n = 310$ nm, diameter polydispersity parameter $\bar{D}_v/\bar{D}_n = 1.02$ (where $\bar{D}_v$ denotes the volume average diameter), and surface concentration of aldehyde groups $[CHO] = 4.04 \times 10^{-6}$ mol/m^2. HSA (Sigma Cohn fraction V) was used as received. Toluene

(OBR Plock, Poland) was distilled and dried over sodium wires before use. Dichloromethane was distilled and dried over CaH_2.

Modification of the surface of quartz plates

Cleaning

The quartz plates (1 cm × 1 cm) were dipped in approximately 5 ml of an aqueous 5 M solution of KOH for 20 min. Then, they were thoroughly washed with distilled water until the pH of washing medium was neutral. Afterwards the plates were dried in an oven for 3 h at 60 °C. Plates prepared in this way are denoted as plates 0.

Grafting of APTS

Plates 0 were treated with an 8% (v/v) solution of APTS in toluene (approximately 5 ml) for 20 h. Thereafter, these SiO_2-APTS plates were thoroughly washed with 5 ml portions of toluene (four times) and then rinsed with a copious amount of ethanol (5 ml portions). The plates obtained are denoted as plates 1.

Grafting of G5 dendrimers

Plates 1 (SiO_2-APTS) were washed with dichloromethane and then treated with 5 ml G5 solution in this solvent (0.44 g/l) for 3 h. Thereafter, the SiO_2-APTS-G5 plates obtained were thoroughly washed with dichloromethane and ethanol. These plates are named plates 2.

Grafting of Starburst PAMAM dendrimers

Plates 2 (SiO_2-APTS-G5) were treated with 5 ml of a solution of Starburst PAMAM dendrimers in a methanol/ethanol mixture for about 18 h. The solution was prepared by introducing 1.1 ml Starburst PAMAM in methanol into a volumetric flask and adding ethanol up to 10 ml. The SiO_2-APTS-G5-PAMAM plates obtained were washed with ethanol, then with water, and thereafter they were dried and stored under vacuum. These plates are denoted as plates 3.

Attachment of P(SAD) microspheres

Plates 3 (SiO_2-APTS-G5-PAMAM) were dipped in a 1.5% w/v suspension of P(SAD) microspheres for 3 h. The resulting specimens [SiO_2-APTS-G5-PAMAM-P(SAD)] were rinsed with distilled water and dried. The plates obtained are denoted as plates 4. One of them was treated with PAMAM, as indicated above, to attach an additional layer of PAMAM. It was then rinsed with copious amounts of ethanol and dried under vacuum. This plate was denoted as plate 5

Attachment of HSA

One plate 2 (SiO_2-APTS-G5) was incubated in an aqueous solution of HSA (0.512 g/l) for 20 h. The specimen was then thoroughly washed with water and dried under vacuum. In this case the substrate was washed with dichloromethane, ethanol, and also with water prior to protein attachment. This procedure differs slightly from that for grafting G5 dendrimers. Additional washing with water permits the change from organic to aqueous medium necessary for HSA adsorption. This plate is denoted as plate 6.

The structures of plates 1–6 are illustrated schematically in Fig. 1.

X-ray photoelectron spectroscopy

XP spectra were recorded using a VG Scientific ESCALAB MKI system operated in the constant analyzer energy mode. An Al Kα X-ray source was used at a power of 200 W (20 mA and 10 kV) and the pass energy

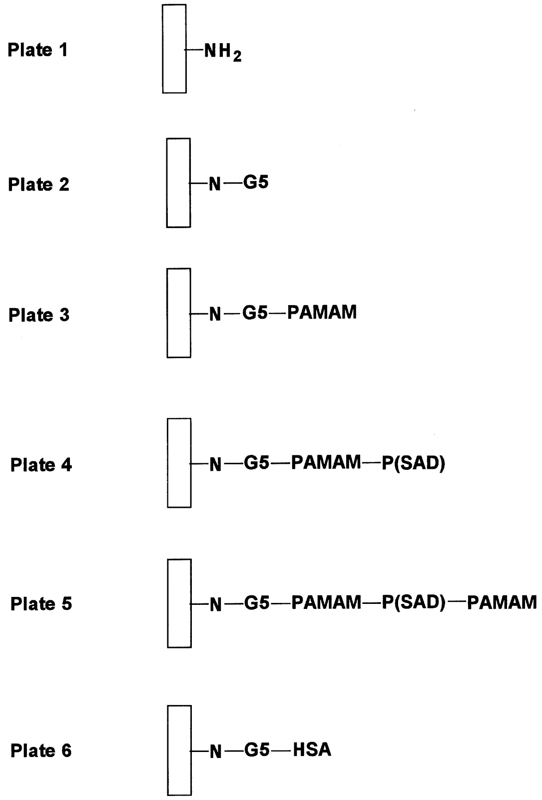


Fig. 1 Schematic illustration of the structures of modified quartz plates

was set at 20 eV. The pressure in the analysis chamber was about 5×10^{-8} mbar. The quartz plates were analyzed at 0° relative to the surface normal. Digital acquisition was achieved with a Cybernetics system and data were collected with a personal computer. Data processing software written by one of us (M.D.) was used for linear Shirley background removal, static charge referencing, peak fitting, and quantification. Charge referencing was determined by setting the main C1*s* CC/CH component at 285.0 eV. We mainly used Gaussian peaks to fit the experimental signals unless a degree of Lorentzian shape was necessary (usually less than 15%). The surface composition (in atom percent) of the various samples was determined by considering the integrated peak areas and their respective experimental sensitivity factors. The atomic concentration (C_x) of any element x is calculated by

$$C_x = \frac{(I_x/s_x)}{\sum(I_x/s_x)} 100\% \ , \tag{1}$$

where I_x and s_x are the integrated peak areas and the sensitivity factors for element x, respectively.

Contact-angle measurements

Contact-angle measurements of drops of water deposited on the plates investigated were performed using a Rhame Hart contact-angle goniometer equipped with an environmental chamber allowing the isolation of the sample from the environment and control of the sample temperature.

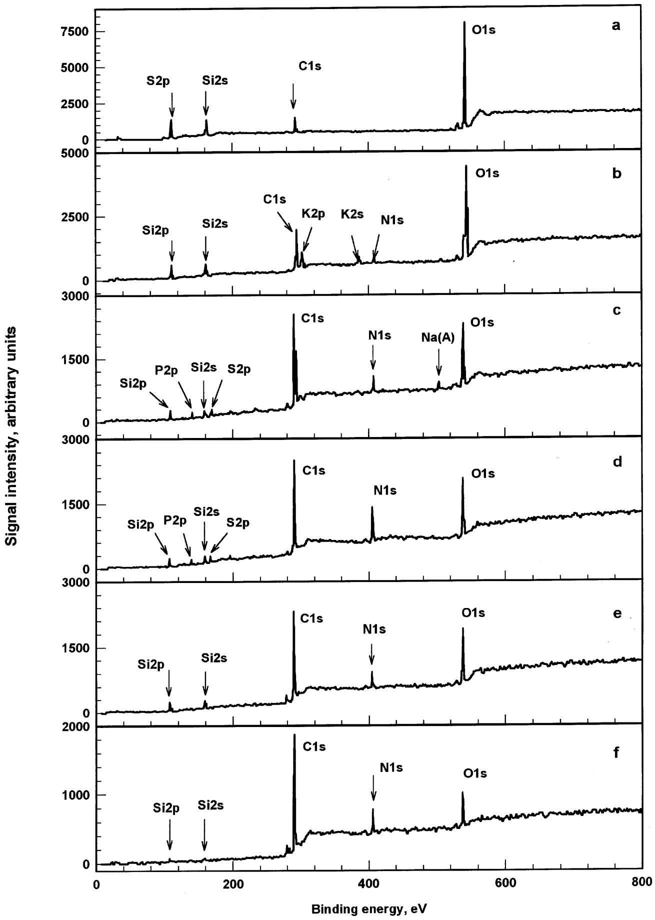


Fig. 2 X-ray photoelectron spectroscopy (XPS) spectra of **a** plate 0, **b** plate 1, **c** plate 2, **d** plate 3, **e** plate 4, and **f** plate 5

Results and discussion

Figure 2 depicts XPS survey scans for KOH-treated quartz plate (plate 0, Fig. 2a) and its modification by APTS, G5, PAMAM, and P(SAD) microspheres (Fig. 2b–f).

It is worth noting that a signal related to carbon atoms (C1*s*) was detected for plate 0. This signal could be attributed to adventitious contamination of the surface of plate 0 with some carbon-containing compound. However, because the conclusions of our studies were based on changes in the intensities of signals other than those of carbon atoms (namely, on signals of Si and P) this contamination was not important. Modification of the surface of the quartz was monitored by detection of the N1*s* signal and a slight increase in intensity of the C1*s* signal (Fig. 2b). In the case of plate 1 surface contamination by potassium was evidenced by the K2*p* and the K2*s* features. Grafting of G5 dendrimer on the APTS-modified quartz surface (formation of plate 2) was indicated by the P2*p* and S2*p* diagnostic peaks shown in Fig. 2c and centered at 134.2 and 162.5 eV, respectively. These binding energies are consistent with a P=S functional group [32] and are in an agreement with a recent XPS study of phosphorus-containing dendrimers [33]. Sodium contamination was also evidenced for plate 2 by the Na Auger peak centered at about 500 eV. When plate 2 was treated with PAMAM, leading to plate 3, the survey of the resulting surface indicated a substantially more intense N1*s* signal (Fig. 2d) relative to that of plate 2. After attachment of P(SAD) microspheres (Plate 4) the N1*s* signal due to G5 dendrimers strongly decreased since these microspheres are nitrogen-free (Fig. 2e). However, the detection of the Si2*p* signal is an indication that the surface of plate 4 was only partially covered with microspheres. This conclusion is based on the fact that Si2*p* photoelectrons were detected although they have an escape depth of about 10 nm which is much smaller than the diameter of the microspheres (310 nm).

The second attachment of PAMAM onto the microspheres (formation of plate 5) results in very strong depletion of Si2*p* and Si2*s* as well as S2*p* and P2*p* signals from the quartz substrate due to the G5 dendrimers (Fig. 2f). It is also interesting to note that the N1*s*/O1*s* intensity increases again due to the second deposition of PAMAM dendrimers. Most probably, PAMAM dendrimers were attached to the aldehyde groups on the surface of the layer of G5 dendrimers not covered during the first exposure to PAMAM and to the exposure to microspheres. This is a further evidence that the P(SAD) microspheres did not fully coat (either by chemical or physical attachment) Plate 3.

Data on the surface chemical composition (in atom percent) of various modified quartz plates analyzed by XPS are collected in Table 1.

The dependence of the fraction of Si atoms in the surface layer on the method of surface layer modification is shown in Fig. 3. It is evident that the relative proportion of silicon readily decreased when the plates were treated with APTS and subsequently with additional layers of dendrimers and microspheres. It is also interesting to note the continuous attenuation of phosphorus signals due to the G5 dendrimers, depicted in Fig. 4, when additional overlayers of PAMAM dendrimers and P(SAD) microspheres were attached to plate 2.

From the attenuation of the intensity of Si2*p* (related to quartz) and P2*p* (due to G5 dendrimers) it was possible to assess the average thickness of G5 in plate 2, PAMAM and G5–PAMAM in plate 3, P(SAD) microspheres in plate 4, and PAMAM microspheres in plate 5. This was done using the Beer-Lambert equation:

$$I = I_0 \exp(-d/\lambda \cos\theta)\ , \tag{2}$$

where I_0 and I denote the intensity of the corresponding signal before and after attenuation, respectively, d denotes the thickness of the overlayer to be determined, λ the elastic mean free path of photoelectrons used to determine d, and θ the photoelectron take off angle relative to the normal to the surface ($\theta = 0°$ in the present work). If a given substrate is only partially covered with an overlayer, a degree of coverage α has to be taken into account resulting in changing Eq. (2) to the following one:

$$I = \alpha I_0 \exp(-d/\lambda \cos\theta) + (1-\alpha) I_0 \tag{3}$$

Equation (3) is useful in the case of plates 3 and 4 for which the degree of coverage of the substrate by PAMAM dendrimers and by P(SAD) microspheres has to be assessed. The value of the parameter λ (for Si2*p* and P2*p* photoelectrons) was calculated using the equation of Seah and Dench [34]:

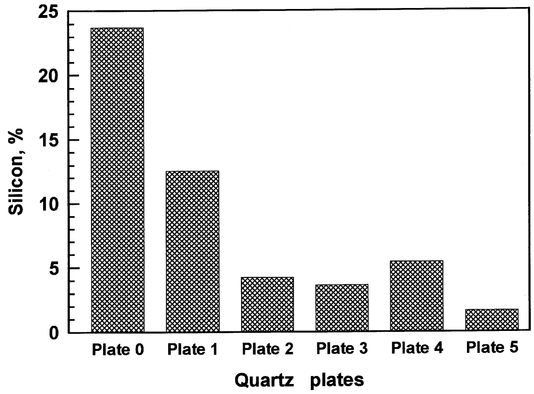


Fig. 3 Atom percent of silicon atoms in the surface layer of modified quartz plates

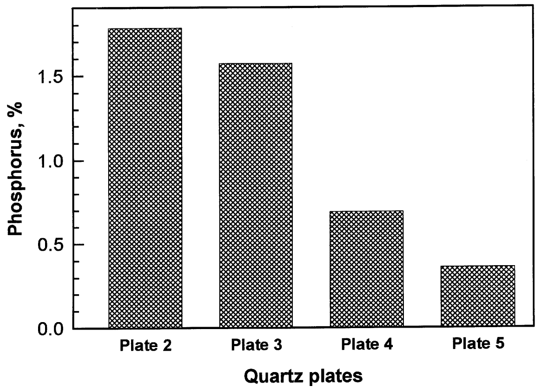


Fig. 4 Atom percent of phosphorus atoms in the surface layer of modified quartz plates

Table 1 Surface chemical composition (in atom percent) of untreated and modified quartz plates

Sample	Si	O	C	N	S	P	K	Na
Plate 0	23.7	53.8	21.9	0.68	–	–	–	–
Plate 1	12.5	36.6	39.6	4.9	–	–	6.4	–
Plate 2	4.2	16.6	65.3	7.1	1.75	1.78	2.4	0.92
Plate 3	3.6	14.4	64.4	14.7	1.3	1.57	–	–
Plate 4	5.4	16.4	70.4	6.6	0.5	0.69	–	–
Plate 5	1.6	8.6	80.6	8.2	0.35	0.36	–	0.27
Plate 6	6.9	24.7	54.8	12.9	0.4	0.29	–	0.06

$$\lambda = 0.11E_{\mathrm{K}}^{0.5} + 49E_{\mathrm{K}}^{-2}\ \mathrm{mg/m^2}\ , \quad (4)$$

where E_{K} is the kinetic energy of the escaping photoelectron (in eV) crossing the overlayer whose thickness is to be determined. In our studies ($E_{\mathrm{K}} > 1000$ eV) the second term in Eq. (4) is negligibly small and λ was computed using the first term only. To convert λ into nanometer units it is necessary to know the density of the overlayer. In our studies we assumed that that the density of dendrimers and microspheres is close to 1.2 g cm^{-3}. Thus, for Al Kα λ was estimated to be close to 3.4 nm for both Si2*p* and P2*p* photoelectrons and the escape depth (3λ) was estimated to be close to 10.2 nm.

Values characterizing the average thicknesses of the G5 and the PAMAM dendrimer layers and of the P(SAD) microspheres are collected in Table 2. It is interesting to note that the average thickness of the G5 dendrimer layer is 3.7 nm and is close to the dimensions of single macromolecules with a similar molecular mass.

For example, in the case of PAMAM G4 and G5 dendrimers with molecular masses equal to 14 600 and 29 100 (molecular mass of G5 dendrimers equals 31 300) the molecular diameters (2R_{g}), determined by small angle X-ray Scattering (SAXS) were 3.4 and 4.7 nm, respectively [35]. On the other hand, the average thickness of the overlayer of PAMAM dendrimers on plate 3 was about one order of magnitude lower (0.35 and 0.29 nm calculated on the basis of the attenuation of the Si2*p* and P2*p* signals, respectively). Apparently the effectiveness of the attachment of PAMAM dendrimers is lower than in the case of G5 ones and instead of Eq. (2) we have to use Eq. (3) for analysis of the XPS data. However, when plate 4 was modified with PAMAM the thickness of the PAMAM adlayer (cf. Table 2, sample plate 5, reference substrate plate 4, peak used P2*p*) estimated by Eq. (2) was 3.2 nm, i.e., was very close to the diameter of PAMAM G4 dendrimers determined by SAXS [35]. Assuming that the thickness of the PAMAM monolayer is 3.2 nm we used Eq. (3) to estimate the degree of coverage of the surface in plate 3 with PAMAM dendrimers from the attenuation of the intensity of the Si2*p* signal (plate 3 versus reference plate 2). The degree of coverage was found to be 0.16.

The average thickness of the layer of microspheres, estimated on the basis of the attenuation of the P2*p* signal, when comparing P2*p* signals of plates 4 and 3, was found to be 3.1 nm. The total average thickness of the bilayer of PAMAM dendrimers and P(SAD) microspheres was calculated from the ratio of the intensities of the P2*p* signals in the spectra of plates 4 and 2 (0.402) to be 3.4 nm. On the other hand, we know that the diameter of the P(SAD) microspheres is 310 nm and, thus, is much greater than the thickness estimated using Eq. (2). This disagreement indicates that Eq. (2) is not valid and that, like PAMAM dendrimers in plate 3, microspheres cover the surface of plate 4 only partially. Thus, we used Eq. (3) to analyze the data. Taking into account that the diameter of the P(SAD) microspheres is 310 nm and remembering that λ is 3.4 nm it was clear that the first term on the right side of Eq. (3) is negligibly small [$\exp(-310/3.4) \approx 10^{-40}$] and can be omitted. Eventually, using the modified Eq. (3) [without the first term proportional to $\exp(-\mathrm{d}/\lambda\cos\theta)$] we calculated the parameter α (the degree of coverage of plate 4 with microspheres) to be 0.60. This result is in agreement with the studies of irreversible attachment (e.g., by covalent immobilization or irreversible adsorption) of microspheres to surfaces showing that in these systems the degree of coverage never exceeds 62% [36–39] and that the complete screening of the surface with microspheres would be possible only in the case of multilayered, usually not controlled, coverage.

The data in Table 1 also indicate that exposure of plate 2 to a solution of HSA, leading to plate 6, results in a significant percentage increase of nitrogen atoms present in protein macromolecules and in a percentage decrease of sulfur and phosphorus atoms. The sulfur atom content in HSA is very low (about 1%) and phosphorus atoms are absent in macromolecules of this

Table 2 Approximate average thicknesses of G5, PAMAM, and P(SAD) microsphere overlayers for some of the quartz plates. See text for explanation of the abbreviations

Overlayer	Sample	Reference substrate	Peak used	Average thickness (nm)
G5	Plate 2	Plate 1	Si2*p*	3.7
PAMAM	Plate 3	Plate 2	Si2*p*	0.35
PAMAM	Plate 3	Plate 2	P2*p*	0.29
G5 + PAMAM	Plate 3	Plate 1	Si2*p*	4.09
P(SAD)	Plate 4	Plate 3	P2*p*	3.1
G5 + PAMAM + P(SAD)	Plate 4	Plate 1	Si2*p*	4.1
PAMAM + P(SAD)	Plate 4	Plate 2	P2*p*	3.4
PAMAM	Plate 5	Plate 4	P2*p*	3.2
P(SAD) + PAMAM	Plate 5	Plate 3	P2*p*	6.3
PAMAM + P(SAD) + PAMAM	Plate 5	Plate 2	P2*p*	6.6
G5 + PAMAM + P(SAD) + PAMAM	Plate 5	Plate 1	Si2*p*	8.2

protein. Thus, the higher percentage of nitrogen and the lower percentage of sulfur and phosphorus atoms indicates that macromolecules of HSA were attached to the surface of plate 2, partially screening the monolayer of G5 dendrimers. Further evidence for HSA attachment is given by the C1*s* high-resolution scans for bulk HSA and for plate 6 (cf. Fig. 5). A prominent C1*s* component centered at about 288.1 eV, due to the peptide linkages of HSA, is also present in the spectrum for plate 6.

The wettability of plates with various surface compositions was determined by contact-angle measurements using a sessile drop method. In these experiments water was used as the reference liquid. The advancing and receding contact angles were measured. The data are collected in Table 3.

As could be expected, the nontreated quartz plates were hydrophilic, apparently due to the presence of SiOH groups at their surfaces (low values of the advancing and receding contact angles). The value of the advancing contact angle was higher, by 17°, than that of the receding one, indicating modification of the quartz surface presumably by strong hydrogen bonding of water molecules. Modification of quartz plates with APTS (yielding plate 1) resulted in significant lowering of their wettability (higher values of θ). Subsequent exposure of plate 1 to contact with G5 dendrimers only slightly decreased the wettability of the plate. Apparently, in spite of the presence of hydrophilic thiophosphate groups in G5 dendrimers the large number of aromatic linkages reduces the hydrophilicity of the surface covered with these macromolecules. The marked increase in wettability was noticed after exposure of plate 2 to PAMAM dendrimers, indicating that these hydrophilic macromolecules, with 64 primary amino groups at the periphery of each of them, were attached to the plate 2 support. Subsequent attachment of P(SAD) microspheres resulted in the creation of a highly hydrophobic surface. It is worth noting that on all plates we clearly noticed marked hysteresis of contact angles. Apparently when surfaces of these plates were in contact with water some modification, e.g., by binding water molecules to amino groups and/or to aldehyde groups at the outer shell of dendrimers [also possible in the case of plates modified by attachment of P(SAD), due to only partial coverage of the surface with microspheres] results on marked increase of their wettability.

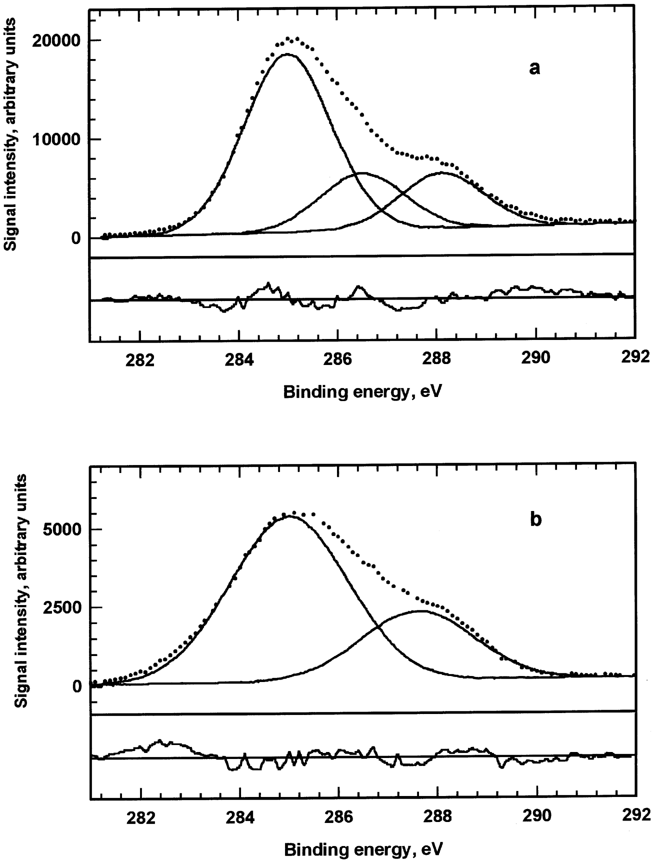


Fig. 5 C1*s* signals in high resolution XPS scans for **a** plate 6 and **b** for bulk human serum albumin

Table 3 Contact angle for quartz plates modified by attachment of APTS, dendrimers (G5 and PAMAM), and P(SAD) microspheres[a]

Sample	Contact angle (deg)	
	Advancing	Receding
Plate 0	40 ± 1	23 ± 2
Plate 1	72 ± 2	54 ± 3
Plate 2	73 ± 3	50 ± 1
Plate 3	60 ± 3	41 ± 1
Plate 4	87 ± 3	61 ± 2

[a] Water was used as the liquid

Conclusions

Subsequent exposure of quartz plates to solutions of APTS dendrimers with CHO and/or NH_2 groups, and to suspensions of P(SAD) microspheres allows the controlled modification of these surfaces by attachment of not more than one monolayer at each step. In the case of microspheres the degree of coverage of the surface close to the maximum predicted by theory was obtained (0.60 and 0.62, respectively). The procedures proposed are suitable for obtaining quartz plates with surfaces modified with layers of molecular, macromolecular, and hundreds of nanometer-sized structures equipped with reactive amino and aldehyde groups suitable, for example, for protein immobilization.

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References

1. Tamaru K (1995) Dynamic processes on solid surfaces. Plenum, New York
2. Twigt F, Piet P, German AL (1991) Eur Polym J 27:939
3. Pye EK, Chance B (1976) Methods Enzymol 44:357
4. Weetall HH, Pitcher WH Jr (1986) Science 232:1396
5. Burg K, Mauz O, Noetzel S, Sauber K (1988) Angew Makromol Chem 157:105
6. Basinska T, Slomkowski S (1995) Colloid Polym Sci 273:431
7. Sequeira CAC (1990) In: Linford RG (ed) Electrochemical science and technology – 2. Elsevier, London, p 319
8. Slomkowski S, Kowalczyk D, Trznadel M (1995) Trends Polym Sci 3:297
9. Ouali L, Stoll S, Pefferkorn E, Elaissari A, Lanet V, Pichot C, Mandrand B (1995) Polym Adv Technol 6:541
10. Miksa B, Wilczynska M, Cierniewski C, Basinska T, Slomkowski S (1995) J Biomater Sci Polym Ed 7:503
11. Bastos-Gonzalez D, Ortega-Vinuesa JL, de las Nieves FI, Hidalgo-Alvarez R (1995) J Colloid Interface Sci 176:232–239
12. Kowalczyk D, Marsault J-P, Slomkowski S (1996) Colloid Polym Sci 274:513
13. Plate NA, Chupov VV (1994) Vysokomol Soedin 36:1862
14. Chiang C-H, Liu N-I, Koenig JL (1982) J Colloid Interface Sci 86:26
15. Park JM, Andrade JD (1988) In: Andrade JD (ed) Polymer surface dynamics. Plenum, New York, pp 67–88
16. Kowalczyk D, Slomkowski S, Chehimi MM, Delamar M (1996) Int J Adhesion Adhesives 16:227
17. Gauthier S, Aime JP, Bouhacina T, Attias AJ, Desbat B(1996) Langmuir 12:5126
18. TanahashiT, Kawaguchi M, Honda T, Takahashi A (1994) Macromolecules 27:606
19. Woodhouse KA, Brash JL (1994) J Colloid Interface Sci 164:40
20. Braithwaite GJC, Howe A, Luckham PF (1996) Langmuir 12:4224
21. Rebar VA, Santore MM (1996) Macromolecules 29:6273
22. Margel S, Dolitzky Y, Sivan O (1992) Colloids Surf 62:215
23. Denkov ND, Velev OD, Kralchevsky PA, Ivanov IB, Yoshimura H, Nagayama K (1992) Langmuir 8:3183
24. Bafaluy J, Senger B, Voegel J-C, Schaaf P(1993) Phys Rev Lett 70:623
25. Micheletto R, Fukuda H, Ohtsu M (1995) Langmuir 11:3333
26. Bar G, Rubin S, Cutts RW, Taylor TN, Zawodzinski TA Jr (1996) Langmuir 12:1172
27. Liu Y, Bruening ML, Bergbreiter DE, Crooks RM (1997) Angew Chem Int Ed Engl 36:2114
28. Launay N, Caminade A-M, Lahana R, Majoral J-P (1994) Angew Chem Int Ed Engl 33:1589
29. Galliot C, Prévoté D, Caminade A-M, Majoral J-P (1995) J Am Chem Soc 117:540
30. Salny M, Bardaji M, Casanove MJ, Caminade A-M, Majoral J-P, Chaudret B (1995) J Am Chem Soc 117:9764
31. Slomkowski S, Miksa B, Trznadel M, Kowalczyk D, Wang FW (1996) Polym Prep Am Chem Soc Div Polym Chem 37:747
32. Wagner CD, Riggs WM, Davis LE, Moulder JFMuilenberg GE (1979) Handbook of X-ray spectroscopy, Perkin Elmer, Eden Praire, MN, p. 52
33. Demathieu C, Chehimi MM, Lipskier J-F, Caminade A-M, Majoral J-P Appl Spectrosc (in press)
34. Seah MP, Dench WA (1979) Surf Interface Anal 1:2
35. Bauer BJ, Topp A, Prosa TJ, Amis EJ, Yin R, Quin D, Tomalia DA (1997) Polym Mat Sci Eng 77:87
36. Schaaf P, Talbot J (1989) J Chem Phys 91:4401
37. Jullien R, Meakin P (1992) J Phys A 25:L189
38. Adamczyk Z, Siwek B, Zembala M, Beloushek P (1994) Adv Colloid Interface Sci 48:151
39. Trznadel M, Slomkowski S (1996) Colloid Polym Sci 274:1109