Synthesis and Characterization of Novel Organic/Inorganic Hybrid Material with Short Peptide Brushes Generated on the Surface

Florin Bucatariu,[†] Ecaterina Stela Dragan,*,[†] and Frank Simon[‡]

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41 A, RO-700487 Iasi, Romania, and Leibniz Institute of Polymer Research, D-01069 Dresden, Germany

A novel route to synthesize an organic/inorganic hybrid material containing short peptide chains attached on the surface (e.g., oligo(S-benzyl-L-cysteine)) was developed. Poly[N-(β-aminoethylene)acrylamide] (PAEA) adsorbed onto silica particles surface (main diameter between 15 and 40 μm) was irreversibly fixed by the reaction between the accessible primary amino groups of the PAEA and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTCDA). After the deposition of PAEA from a salt-free aqueous solution onto microporous silica particles and stabilization by a cross-linking reaction with BTCDA, five repeated coupling reactions of boc-S-benzyl-L-cysteine were performed. Changes in surface charges during the polyelectrolyte adsorption were studied by electrokinetic measurements. The cross-linking degree was a tool to control the surface charge of the PAEA/silica hybrid particles. X-ray photoelectron spectroscopy (XPS) was employed to obtain information about the amount of the adsorbed polyelectrolyte as well as the amount of the amino acid S-benzyl-L-cysteine that was covalently bound to the hybrid particle surface and polycondensed there. In the XPS spectra, the sulfur peaks (S 2p$_{3/2}$, S 2p$_{1/2}$, and S 2s) qualitatively and quantitatively indicated the presence of the amino acid on the hybrid material surface. After each step of coupling, the intensity of the S 2s peak was increased by a constant value. This indicates the oligopeptide growth. The novel hybrid material offers possibilities for subsequent derivatization reactions such as coupling other amino acids, peptides, obtaining hybrid ion exchange resins, and so forth.

I. Introduction

The adsorption of polyelectrolytes onto various kinds of solid materials[1–9] is a rapid growing field of tremendous importance for colloidal science, biophysics, nanoelectronics, and so forth. Indeed, many practical systems for industrial applications utilize various polyelectrolytes as stabilizing agents, emulsifiers, rheology modifiers, and agents for nanofabrication because of their remarkable adsorption properties. Concerning the nanofabrication, Decher et al.[10] developed a new technology for synthesizing stable polyelectrolyte multilayers. The authors used oppositely charged polyelectrolytes that had been adsorbed consecutively from the diluted aqueous solutions onto flat surfaces. Möhwald et al.[11,12] used similar techniques for the synthesis of novel polymeric hollow spheres. The polyelectrolytes usually used have been poly(sodium 4-styrene sulfonate) and quaternary polyammonium salts (i.e., strong polyelectrolytes), which seem unsuitable for further functionalization reactions under mild conditions.

The presence of reactive groups such as primary amino and carboxylic groups is a prerequisite for further functionalization reactions. Thus, Spange et al.[13–18] produced stable poly(vinyl formamide-*co*-vinyl amine) [P(VFA-*co*-VAm)]/inorganic oxide hybrid particles. Various procedures such as grafting-to, grafting-from, cross-linking surface polymerization, and subsequent functionalization of the adsorbed P(VFA-*co*-VAm) chains have been used to vary the surface functionalities. The P(VFA-*co*-VAm) was adsorbed from aqueous solutions onto silica and titanium dioxide particles.[16,17] The authors used fullerene[16] and (4,4′-diisocyanate)diphenyl methane[17] to irreversibly fix the polyelectrolyte layer onto the particle surfaces. It was shown that P(VFA-*co*-VAm) is a highly interesting polyelectrolyte for the surface functionalization of inorganic particles because, after the surface modification, a large number of reactive primary amino groups remain available for subsequent functionalization reactions. Bringley et al.[19] obtained nanoparticle/polyelectrolyte colloidal assemblies with enhanced colloid stability at physiological pH and ionic strength, with possibilities for bioconjugation and nanocarriers for in vivo applications. The immobilization of a hydrophilic and sometimes stimuli-responsive layer as well as the possibility of coating particles with specific ligands (saccharide moieties, lipids, biomolecules) open very attractive potentialities.[20,21]

The aim of this article was first to investigate the adsorption of poly[N-(β-aminoethylene)acrylamide] (PAEA) onto silica particles and the stability of the adsorbed layer under mechanical stress, and second to demonstrate that the adsorbed PAEA contains an adequate number of accessible primary amino groups in the side chains to be adequate for subsequent derivatization reactions with electrophilic reagents. A cross-linking reaction with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTCDA) and step-by-step coupling reactions of boc-S-benzyl-L-cysteine on the PAEA/silica hybrid were performed.
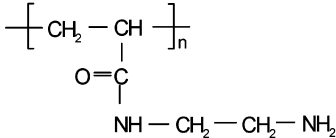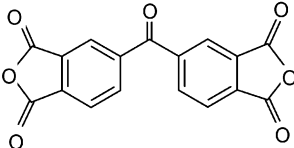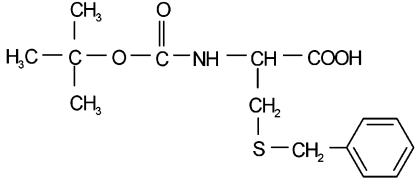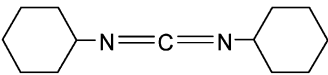
II. Materials and Methods

II.1. Materials. Kieselgel 60 (Merck, Darmstadt, Germany), a commercially available spherical silica, was used as inorganic substrate material. The main diameter of the microporous silica particles ranged

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* Corresponding author. Telephone number: +40.2322217454. Fax number: +40.232211299. E-mail: sdragan@icmpp.ro.

† "Petru Poni" Institute of Macromolecular Chemistry.

‡ Leibniz Institute of Polymer Research.

Chart 1. Structures of the Polycation PAEA, the Cross-Linker BTCDA, and the Amino Acid Boc-*S*-benzyl-L-cysteine Used to Produce Peptide-Functionalized Hybrid Particles

poly[N-(β-aminoethylene)acrylamide] (PAEA)	3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTCDA)
boc-S-benzyl-L-cysteine	dicyclohexylcarbodiimide (DCC)

between 15 and 40 μm. The distribution of the pore diameters had a maximum in the range of 4−6 nm. The PAEA was synthesized by an aminolysis−hydrolysis reaction with 1,2-diaminoethane, converting the nitrile groups of polyacrylonitrile into the amino-terminated structure shown in Chart 1. The synthesis was described in detail in a previous paper.[22] BTCDA, *N*,*N*′-dicyclohexyl carbodiimide (DCC, Merck, Darmstadt, Germany), and boc-*S*-benzyl-L-cysteine (Fluka, Germany) were used as received. The structures of all reagents are summarized in Chart 1.

II.2. Adsorption Procedure and Cross-Linking. In order to vary the PAEA concentration for the adsorption experiments, an aqueous salt-free stock solution containing 10^{-2} mol·L^{-1} PAEA was diluted to 0.97×10^{-3} to 3.51×10^{-3} mol·L^{-1}. Samples of 0.5 g of silica were suspended in the diluted PAEA solutions. During the adsorption process over 3 h, the suspension was gently shaken at room temperature. The modified particles were filtered off by slight suction. The hybrid materials were carefully washed with distilled water and dried in vacuum at 40 °C for 24 h.

The cross-linking reaction of the PAEA layer adsorbed onto the silica particles was carried out using BTCDA as the cross-linker. For this purpose, the hybrid particles were suspended in acetone. Then, 0.02, 0.10, or 0.50 w/w% BTCDA (w/w% = weight of BTCDA per gram PAEA/silica × 100%) was added. The suspension was gently shaken at room temperature for 3 h. After filtering and washing, the hybrid particles were dried in vacuum at 40 °C for 24 h.

II.3. Generation Procedure of the Short Peptide Brushes. The functionalization of the cross-linked hybrid material with *S*-benzyl-L-cysteine was carried out according to the procedure used by Merrifield.[24] For the coupling reaction of the protected amino acid, 2 g of the PAEA/silica hybrid particles cross-linked with BTCDA was suspended into a solvent mixture formed by 10 mL of dichloromethane (DCM) and 10 mL of dimethylformamide (DMF). After 10 min, a solution containing 0.200 g (0.64 mmol) of boc-*S*-benzyl-L-cysteine in 4 mL of DCM was added and shaken for 10 min. Then, a solution of 0.132 g of DCC (0.64 mmol) in 2 mL of DCM was added, and the suspension was shaken for 3 h. The hybrid particles were filtered and washed three times with 10 mL of DMF and three times with 10 mL of DCM to remove the excess of reagents and byproducts. For the deprotection reaction of the protected amino acid coupled to the silica hybrid particles, the reaction with 3 g of trifluoroacetic acid (TFA) in 10 mL of DCM was carried out. After deprotection, the hybrid particles were filtered and washed with 2 mL of triethylamine in 10 mL of DCM and three times with 10 mL of DCM.

II.4. Characterization Methods. Potentiometric titrations were performed with the particle charge detector PCD 02 (Mütek, Germany) between pH 3.5 and 10, using 0.1 mol·L^{-1} KOH and HCl, respectively.

Total organic carbon (TOC) analysis is a method to indirectly measure the adsorbed polymer amount by determining the amount of carbon in the supernatant solution. The TOC analysis was performed using the TOC 5000-A (Shimadzu of Kyoto, Japan), oxidizing the carbon to CO_2 and measuring the gas concentration by its infrared absorption. TOC analysis is effective to measure carbon concentrations of over 15 ppm (equivalent to about 0.005% of polymer per sample).

The electrokinetic measurements were performed as streaming potential experiments employing an electrokinetic analyzer (EKA, Anton Paar, Austria). In a specially designed powder-measuring cell,[11] the hybrid materials were packed as a diaphragm, which was flown through by an aqueous KCl solution ($c = 0.001$ mol·L^{-1}). The pH dependent measurements start from pH = 6.8. The addition of 0.1 mol·L^{-1} HCl lowered the pH values, while the addition of 0.1 mol·L^{-1} KOH increased the pH values. After recording the streaming potential values of the acidic pH range, the sample was exchanged for measuring the streaming potential values in the basic pH range. The values of the apparent electrokinetic potential (zeta potential, ζ) were calculated from the measured streaming potential values according to the Smoluchowski equation:[23]

$$\zeta = (\eta/\epsilon_0\epsilon_r)\cdot(\Delta U/\Delta P)\cdot\kappa \qquad (1)$$

where ζ is the apparent zeta potential, ΔU is the streaming potential, Δp is the pressure difference, κ is the conductivity, η is the dynamic viscosity of the KCl solution, ϵ_r is the relative permittivity of the KCl solution, and ϵ_0 is the permittivity of the free space.

X-ray photoelectron spectroscopy (XPS) studies were carried out by means of an Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical, Manchester, U.K.). The spectrometer was equipped with a monochromatic Al Kα (h·ν = 1486.6 eV) X-ray source of 300 W at 15 kV. The kinetic energy of the photoelectrons was determined with a hemispheric analyzer set to a pass energy of 160 eV for wide-scan spectra. During all measurements, electrostatic charging of the sample was overcompensated by means of a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same amount that was necessary to set the C 1s peak to 285.00 eV for saturated hydrocarbons. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function.

III. Results and Discussion

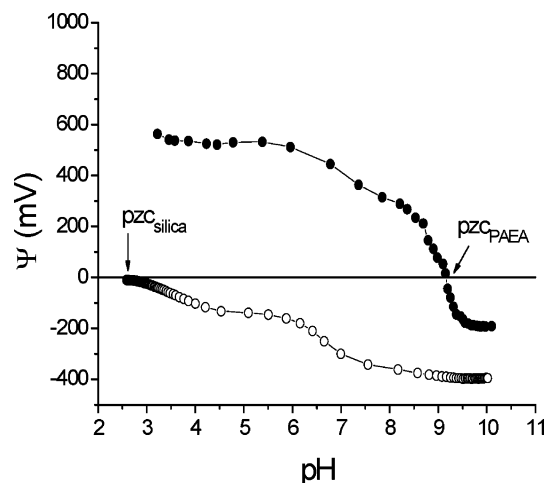**III.1. Characterization of Bare Silica and PAEA.** Silica particles suspended in water or in aqueous solution may be

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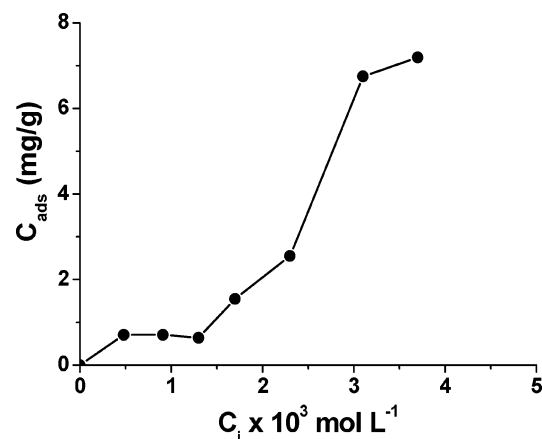**Figure 1.** Potentiometric titration of bare silica (○) and PAEA (●).

Figure 2. Adsorption isotherm of PAEA from aqueous solution (c_i = initial concentration of PAEA in the solution).

Figure 3. Relative amount of PAEA adsorbed onto silica surfaces determined by XPS. The amount of the polyelectrolyte is expressed by the nitrogen content [N], and the number of unoccupied silica surface sites is indicated by the silicon value [Si].

Figure 4. Influence of solution pH on adsorbed amount of PAEA onto silica particles.

considered as a cross-linked polyelectrolyte. The surface charge of the silica particles is either the result of dissociation processes of Brønsted-acidic silanol groups (Si−OH) forming negatively charged silanolate ions (Si−O⁻) or proton adsorption yielding Si−OH₂⁺ species. In a wide range of pH, the two charge generation mechanisms may take place simultaneously on the silica surface because the acidity of surface silanol groups can be quite different. In the presence of hydronium ions, the primary amino groups of PAEA can be protonated (−NH₃⁺). Hence, an important component of the driving force of the adsorption of PAEA onto silica surfaces is the Coulomb force between the oppositely charged centers of the solid surfaces and the polycation chains. Potentiometric titrations in water showed that the point of zero charge (pzc = pH|$_{\Psi=0}$, where Ψ is the potential) was reached at pH = 2.5 for bare silica, and at pH = 9.2 for PAEA (Figure 1).

III.2. Adsorption of PAEA onto Silica and Stability of the Adsorbed Layer. To study the effect of the PAEA concentration on its adsorption onto silica, the concentration was varied in the range of 0.5×10^{-3} to 3.5×10^{-3} mol·L⁻¹. The adsorption of PAEA from salt-free aqueous solution increased with the increase of the PAEA concentration. The results of TOC analysis of the supernatant PAEA solution showed two plateau regions (Figure 2). It was assumed that, besides the adsorption of PAEA onto silica particles, an additional polyelectrolyte self-aggregation occurred by increasing the polyelectrolyte concentration in the solution. Hence, the remaining PAEA content in the supernatant solution appeared smaller.
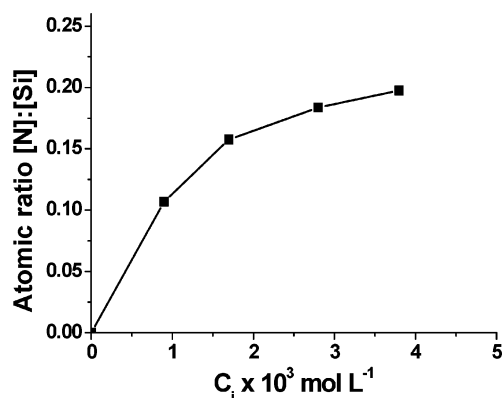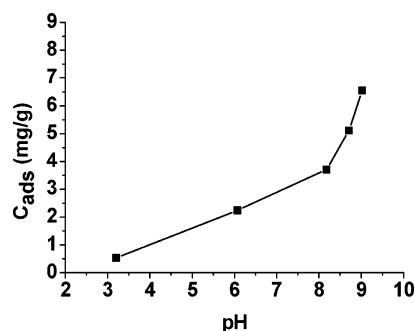
During washing the freshly prepared PAEA/silica hybrid materials, all weakly bound macromolecules are removed. Only the polycation chains that are bound via strong interaction forces remain on the particle surface. The adsorption isotherm, determined from XPS measurements of PAEA/silica hybrid particles (Figure 3), confirming this assumption, showed a clear plateau region. Here, it was assumed that the N 1s peak appeared only from the polyelectrolyte layer, and Si 2p is a specific signal of the substrate material. Then, the atomic ratio [N]:[Si] should be an accurate measure of the amount of adsorbed polyelectrolyte.

Figure 4 shows the influence of the pH value of the solution on the adsorbed amount of PAEA. At low pH values, the macromolecules have a high charge density, and, as a consequence, the chains are stiff and stretched. Hence, the amount of PAEA adsorbed onto the silica surface was low. As has been shown in Figure 1, an increased pH value decreased the charge density of PAEA by de-protonation of the cationic ammonium groups. The electrostatic repulsion between the PAEA chains was diminished, with the macromolecules being more flexible, and, therefore, a higher amount of PAEA was adsorbed onto the silica surface.

The stability of the formed PAEA layer was tested by the streaming potential experiments. To determine the streaming potential, it is necessary to move the test liquid (KCl solution of various pH values) along the sample surface. The streaming liquid with a pressure of 300 mbar in maximum causes a considerable mechanical shear stress on the coated solid surface. Figure 5 shows the apparent zeta-potential values of PAEA/silica hybrid particles as a function of the pH values of the streaming aqueous KCl solution.

In the first measuring cycle, in the pH range 3 < pH < 6, the positive zeta potential remained nearly constant (region A, CDV
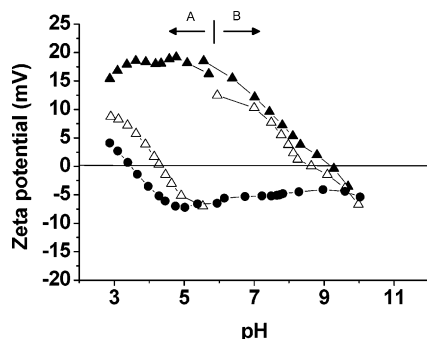
Figure 5. Zeta-potential values determined from streaming potential measurements as a function of the pH of aqueous 0.001 mol·L^{-1} KCl, on bare silica (circles) and PAEA/silica ([N]:[Si] = 0.1837) (triangles): closed symbols − first measurement; open symbols − second measurement of the PAEA/silica hybrid particles.

Figure 5). Here, all amino groups that are able to form positively charged ammonium salt species are protonated. However, the protonated species are water soluble and can be easily removed by the aqueous medium. The streaming liquid removes the soluble polycation chains from the surface and favors the dissolving process by changing the adsorption equilibrium to the side of the solvated species. In order to prove the mechanism mentioned above, the measurements were repeated on the same hybrid material. The open symbols in Figure 5 show that the pretreatment of the sample surfaces in acidic media significantly changed the shape of the function $\zeta = \zeta(pH)$ in the acidic region (region A in Figure 5). The second measurement of the same PAEA/silica sample shows that the isoelectric point (iep = $pH|_{\zeta=0}$) found at iep = 4.2 is much closer to the iep of the bare silica, which is 3.5. That indicated that the adsorbed PAEA layer was unstable under acidic conditions and, therefore, could be easily washed off.

In the basic range (region B), the ammonium species were gradually deprotonated by the excess of HO$^-$ ions in the aqueous solution and, as a consequence, the zeta-potential value decreased. In the first measuring cycle, the iep of the PAEA/silica hybrid excellently agreed with the pzc of the PAEA solution (Figure 1). This confirmed that only hydronium and hydroxy ions determined the surface potential, and indicated that the PAEA fully covered the silica surface and determined the charging behavior of the hybrid material. If the measurement was repeated in basic medium (the sample was not in contact with the acidic solution), the iep of the PAEA/silica hybrid particles was found at iep = 8.6, very closed to the iep obtained for the first measurement, which was iep = 9.4. Obviously, under Brønsted-basic conditions, the adsorbed PAEA layer remained stable on the silica surface. Confirming the discussion above, the N 1s intensities of the wide-scan XPS spectra, clearly showed that the PAEA layer was largely removed during the streaming potential experiments employing Brønsted-acidic solutions (Figure 6).

III.3. Chemical Cross-Linking of Adsorbed PAEA. The instability of the adsorbed polyelectrolyte layers is a substantial disadvantage of the hybrid materials, limiting their applications. One way to stabilize the polyelectrolyte surface layer is the inter- and intramolecular cross-linking of the adsorbed polymer chains. During the cross-linking reaction, a polymer network capturing the silica particle can be formed. In order to cross-link the PAEA chains via a few of their amino groups, BTCDA was used. BTCDA is equipped with two anhydride groups that can link two amino groups belonging to two polymer chains. The idealized structure of the three-dimensional network is depicted in Figure 7.
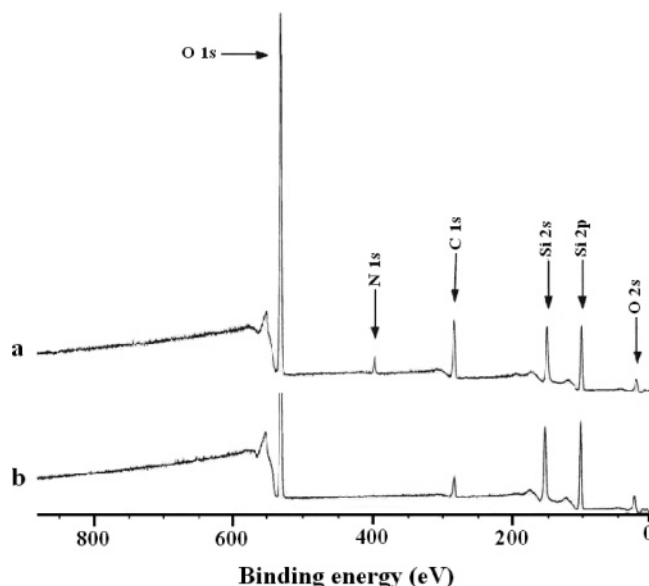

Figure 6. Wide-scan XPS spectra of PAEA/silica hybrid particles ([N]: [Si] = 0.1837) before (a) and after (b) the streaming potential measurements in the acidic range.
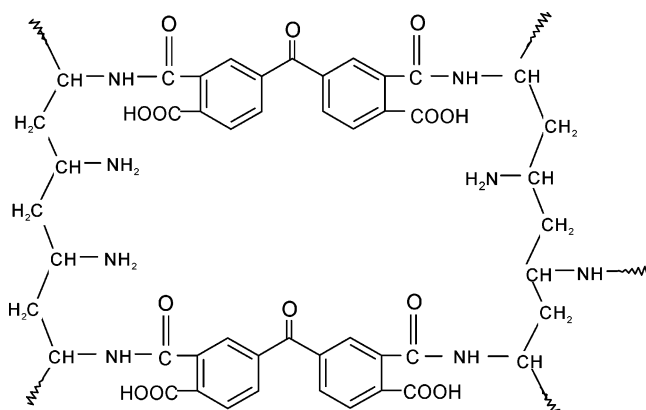

Figure 7. The idealized structure of the PAEA−BTCDA three-dimensional network.
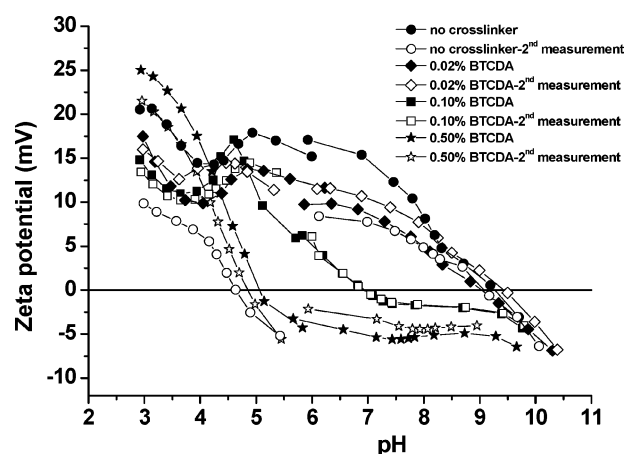

Figure 8. Zeta-potential values determined from streaming potential measurements for non-cross-linked (circles) and cross-linked (diamond, squares, stars, and triangles) PAEA/silica hybrid particles ([N]: [Si] = 0.1837). Each sample was measured two times in the same range of pH: close symbols − first measurement; open symbols − second measurement.

Figure 8 shows the zeta potential of PAEA/silica hybrid material and of PAEA/silica cross-linked with 0.02%, 0.10%, and 0.50% w/w BTCDA (weight cross-linker/weight hybrid
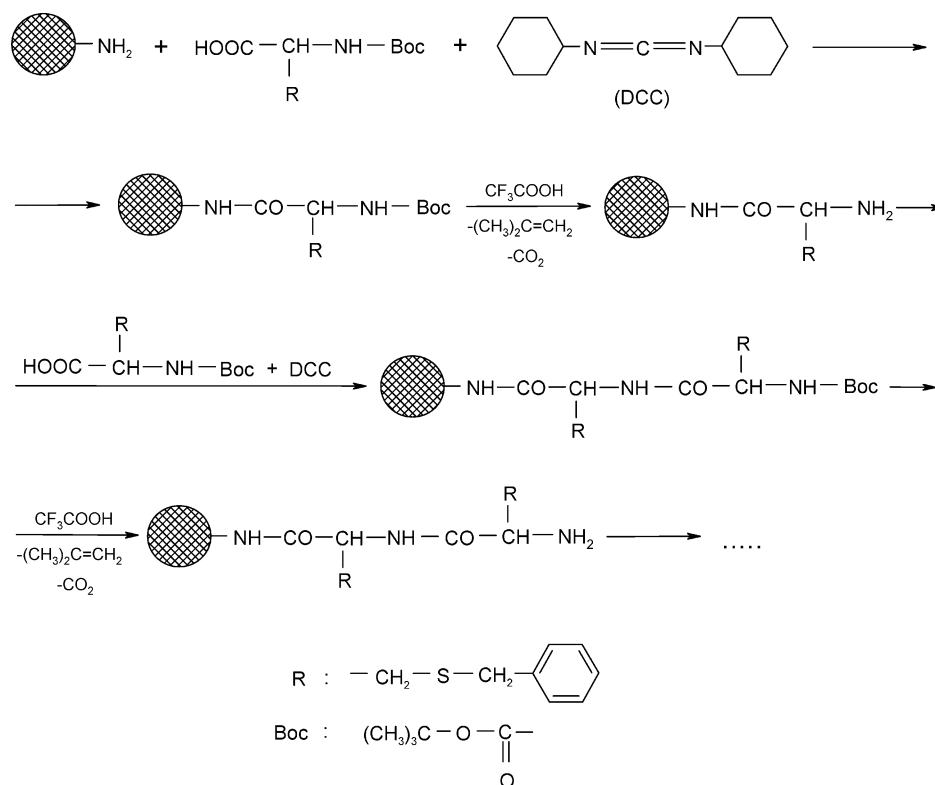
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Figure 9. The step-by-step coupling of boc-*S*-benzyl-L-cysteine onto the surface of PAEA/silica hybrid particles.
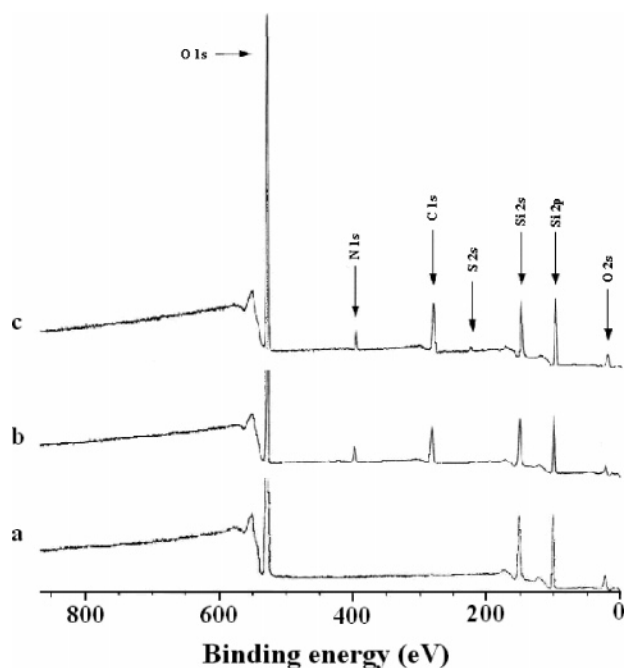

Figure 10. Wide-scan XPS spectra of bare silica (a), PAEA/silica (b), and (PAEA−BTCDA)/silica after the first coupling of boc-*S*-benzyl-L-cysteine (c).

Figure 11. The S 2s XPS spectra of the PAEA/silica particles (a) before the coupling of boc-*S*-benzyl-L-cysteine and (b) after the first, (c) after the third, and (d) after the fifth coupling of boc-*S*-benzyl-L-cysteine. The intensities of the S 2s peaks were related to the intensity of the C 1s peak, which was kept constant.

material $\times$ 100%) as a function of the pH value of the streaming aqueous KCl solution.

The removal of the adsorbed PAEA layer from the silica particle surface of non-cross-linked PAEA/silica hybrid particles was explained above. The iep of the PAEA/silica cross-linked with 0.02% w/w BTCDA measured in the basic range was 9.2, nearly the same as that found for the non-cross-linked sample. This showed that the number of free amino groups from the hybrid surfaces was not significantly affected by the cross-linking reaction at this concentration of BTCDA. However,
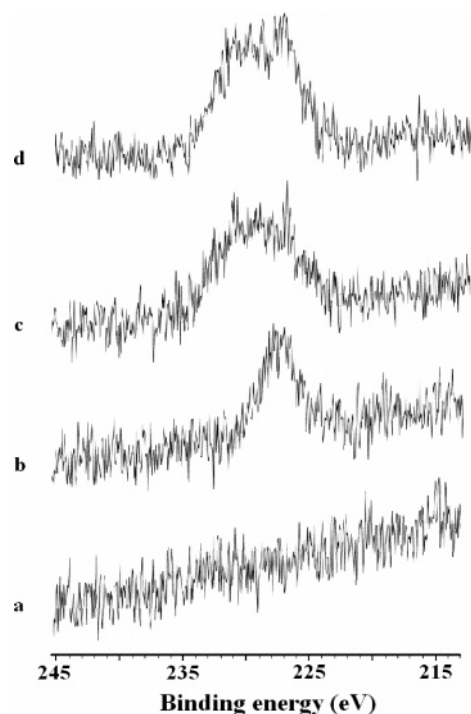
when the measurement was repeated in the acidic pH range, the slightly cross-linked hybrid particles (0.02% w/w BTCDA) showed nearly the same curve ($\zeta = \zeta$(pH)) as that recorded in the first measurement. Obviously, the small amount of BTCDA was able to stabilize the PAEA layer on the silica surface. Using 0.1% w/w BTCDA, a stable PAEA/silica hybrid was obtained. The iep of 6.8 indicated that the number of free amino groups
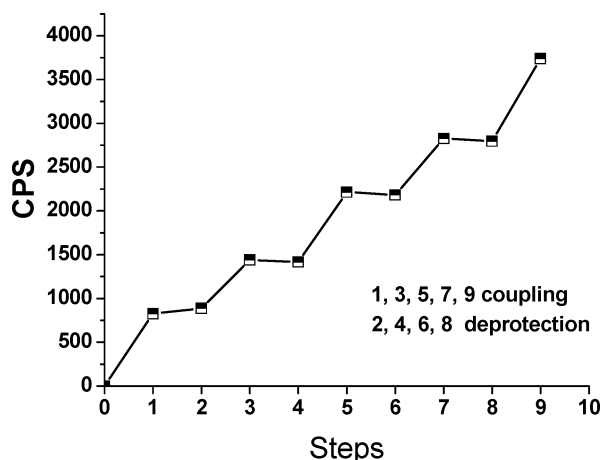
Figure 12. The intensity of the S 2s peaks (CPS = counts per second) after the coupling of boc-*S*-benzyl-L-cysteine and its deprotection reaction. The intensities of the S 2s peaks were related to the intensity of the C 1s peak, which was kept constant.

on the particle surfaces decreased because a considerable number of them were involved in the cross-linking reaction. At 0.50% w/w BTCDA, the iep of the cross-linked hybrid particles was approximately 5, showing that nearly all amino groups from the hybrid particles were converted with the cross-linking agent.

For further surface-functionalization reactions, hybrid particles cross-linked with 0.02% w/w BTCDA were used. These PAEA/silica hybrid materials appeared to be stable and possessed a sufficient number of free amino groups on the hybrid surface, enabling them to form covalent bonds with other compounds.

III. 4. Reaction of Boc-*S*-Benzyl-L-Cysteine with the Free Amino Groups from the Surface of Silica Hybrid Particles. The functionalization of the cross-linked hybrid material with *S*-benzyl-L-cysteine was carried out as shown in Figure 9, where DCC was used as the dehydrating agent.

The successful grafting reaction introduces sulfur in the sample surface, which can be easily detected (as S 2p$_{3/2}$, S 2p$_{1/2}$, and S 2s peaks) and quantified in the XPS spectra (Figure 10). According to the given stoichiometry in Figure 9, the amount of introduced sulfur corresponds with the amino acid's grafting degree.

As expected, the bare silica surface shows intensive peaks of silicon and oxygen, and only small traces of carbon originated from hydrocarbon surface contaminations (Figure 10a). The adsorption of PAEA introduces considerable amounts of carbon and nitrogen. The cross-linking procedure did not significantly affect the elemental surface composition (Figure 10b). As mentioned above, after the grafting of boc-*S*-benzyl-L-cysteine, the S 2s peak can be clearly seen in the XPS spectra (Figure 10c). Its intensity increased step-by-step with stepwise grafting of the amino acid (Figure 11). According to the reaction Scheme in Figure 9, each coupling reaction was followed by a deprotection reaction to produce new free amino groups of the grafted amino acid covalently grafted to the particle surface.

These free amino groups are able to react with the boc-*S*-benzyl-L-cysteine offered in a followed grafting step. After the grafting reaction, the intensity of the S 2p peak increased by the same amount. From this constant increase of the sulfur content, it was concluded that the grafting reactions preferably took place on the pregrafted amino acids. In this way, oligopeptides grow up on the hybrid surface. As can be seen in Figure 12, the deprotection step did not influence the sulfur content on the hybrid surface. This demonstrated that the sample's

treatment with TFA did not decompose the functionalized hybrid material or remove weakly bound species.

IV. Conclusion

The adsorption of PAEA onto silica particles was investigated. Subsequent cross-linking reactions of the accessible primary amino groups of PAEA/silica hybrid particles with BTCDA offered a stable hybrid material containing a reasonable number of reactive amino groups located on the outer surface of the silica, giving possibilities for further derivatization reactions such as the coupling of amino acids to produce oligopeptides. We showed the feasibility of the grafting of boc-*S*-benzyl-L-cysteine on the surface of PAEA/silica hybrid particles to build-up short-chain peptide brushes.

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