Fabrication of Silica Particles Functionalized with Chromophores and Amino Groups Using Synergism of Poly(vinylamine) Adsorption and Nucleophilic Aromatic Substitution with Fluoroaromatics

Isabelle Roth,[†] Frank Simon,[‡] Cornelia Bellmann,[‡] Andreas Seifert,[†] and Stefan Spange*[,†]

Department of Polymer Chemistry, Technical University Chemnitz, Strasse der Nationen 62, D-09101 Chemnitz, Germany, and Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

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Nucleophilic aromatic substitution reactions of fluoronitro-substituted aromatic compounds with poly(vinylamine) (PVAm)/silica adsorbates were studied to equip silica particles with primary amino as well as several chromophoric groups. 4-Fluoronitrobenzene (**1**, 4-FNB), 2-fluoronitrobenzene (**2**, 2-FNB), 4-fluoro-3-nitroaniline (**3**, 4-FNA), *N*,*N*-dimethyl-4-fluoro-3-nitroaniline (**4**, 4-DMFNA), 1-fluoro-2,4-dinitrobenzene (**5**, Sangers reagent, FDNB), 1,5-difluoro-2,4-dinitrobenzene (**6**, DFDNB), 4-fluoro-3-nitroazobenzene (**7**, FNAzoB), *N*-(2′,4′-dinitrophenyl)-4-fluoro-3-nitroaniline (**8**, *N*-DNP-FNA), and 4-fluoro-3,4′-dinitrostilbene (**9**, FDNstilbene) have been used as functionalization reagents. Various chromophoric functionalities could be readily synthesized on the silica surface by this elegant method. The degree of PVAm functionalization with chromophores was determined from the redissolved fraction of the functionalized polymer by means of UV/vis spectroscopy using model compounds as references. The surface structures of the chromophores fixed on polymer-modified silica particles were studied using X-ray photoelectron spectroscopy (XPS) and UV/vis spectroscopy. Brunauer−Emmett−Teller (BET) measurements and XPS studies suggest that the chromophores introduced in the PVAm layer on silica are differently distributed in the adsorbed PVAm layers. The vertical distribution of the chromophore in the PVAm layer depends on the reactivity of the fluoroaromatic. The more reactive the fluoroaromatic, the more unaffected remains the former pore-size distribution of silica. Changes of the surface charge were investigated by means of electrokinetic measurements.

Introduction

There is great demand for the development of pH resistance as well as responsive nanoparticles as UV/vis sensors for environmentally sensitive biomacromolecules and other biologically active compounds under ambient aqueous conditions.[1,2] Furthermore, introduction of pH as well as surface polarity sensitive chromophores is of importance to observe adsorption processes and pH changes by UV/vis spectroscopic techniques, which are also easy to perform in complex systems. For this purpose, an intelligent combination of a water-soluble polymer sensitive in a wide pH range with suitable chromophores is required.

Poly(vinylamine)s (Lupamines, BASF, Ludwigshafen, Germany, PVAm's) are water-borne polymers suitable to adsorb on a variety of materials, which make them promising candidates for this purpose.[3−8] PVAm contains numerous primary amino groups (−NH_2). Depending on the surrounding pH value, the groups can be protonated (−NH_3^+) or present as a charge-neutral amine. Hence, the polymer can be considered as a weak cationic polyelectrolyte. In addition, amino groups are suitable to be chemically functionalized in different ways, because they do react with epoxides, acid anhydrides, aldehydes, and a lot of other reagents.[9−11]

Nucleophilic substitution reactions of fluoroaromatic compounds with PVAm offer a great synthetic potential to directly incorporate chromophoric groups into the polymer backbone.[12−15] The advantage of the nucleophilic aromatic substitution is that a push−pull substituted aromatic system

* Corresponding author e-mail: stefan.spange@chemie.tu-chemnitz.de.
[†] Technical University Chemnitz.
[‡] Leibniz Institute of Polymer Research Dresden; http://www.ipfdd.de.

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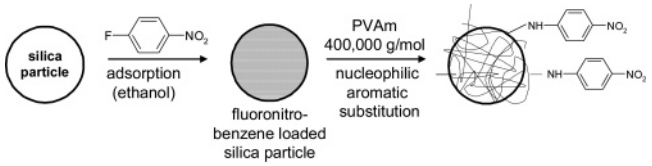
Scheme 1. Reaction of Poly(vinylamine) (PVAm) with Activated Fluoroaromates (e.g., 4-Fluoronitrobenzene) to Form Chromophoric Nitrophenyl Functionalized PVAm Push−Pull Systems Adsorbed onto Silica

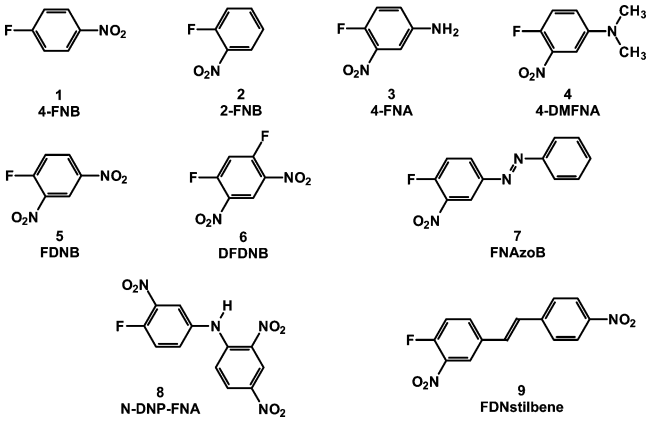


is formed in only one synthetic step.[16,17] The fluoride ion becomes a better leaving group compared to nonsubstituted fluorobenzene with an increasing number of electron-withdrawing groups at the fluorosubstituted phenyl ring.[18,19] Especially, nitro, nitroso, and diazonium groups are suitable to activate the fluoroaromatics for this elegant synthetic route.[17] Scheme 1 exemplarily shows the synthetic route of the reaction of poly(vinylamine)s (PVAm's) with activated fluoroaromatics to form chromophoric nitroaniline functionalized PVAm push−pull systems adsorbed onto silica.

The introduction of nitroaniline derivatives in polymers is of remarkable interest, because these functionalities are widely applied to materials science (NLO)[20,21] and analysis (solvatochromism).[22−27] There are numerous substituted 4-nitroaniline derivatives which are used as solvent-sensitive indicators for creating polarity scales,[22−25] as lipophilic indicators in micelles and bilayers, and in biological membranes. [26,27] Therefore, water-soluble polymers bearing those functionalities are potential candidates for the production of sensor layers and pH-responsive membranes. Another aim is to demonstrate the synthetic potential of this new synthetic approach to functionalize silica particles. Among nitroanilines, a series of fluorosubstituted nitroaromatic compounds containing azobenzene and nitrostilbene derivatives were chosen (Scheme 2).

In contrast to monofluorosubstituted nitroaromatic derivatives, the two fluorine atoms of the difluorosubstituted derivative **6** (1,5-difluoro-2,4-dinitrobenzene) and the activated *ortho*-nitro groups of **5** (1-fluoro-2,4-dinitrobenzene) or **7 (**4-fluoro-3-nitroazobenzene), respectively, are suitable to be substituted by amino groups. Hence, molecular structures of the chromophores directly generated and localized on the particle surface can be various. It is expected that the less reactive monofluorosubstituted nitroaromatic

Scheme 2. Various Fluoroaromatics Used for the Adsorption onto Silica and Subsequent Nucleophilic Aromatic Substitution Reaction with Poly(vinylamine) in Water



derivatives follow the reaction shown in Scheme 1, which can be considered as a model reaction. The bis-functionality of the activated derivatives **5**, **6**, and **7** additionally should allow cross-linking reactions along as well as between PVAm chains.

Fluoroaromatics are usually insoluble in water. Therefore, the nucleophilic substitution reaction with PVAm in water was mediated by a fluoroaromate/2,6-*O*-dimethyl-β-cyclodextrin (β-DMCD) complex, which is readily soluble in water.[12−14]

However, it was shown that cross-linking reactions (in the absence of silica particles) are of minor importance for the reagents **1** (4-fluoronitrobenzene), **2** (2-fluoronitrobenzene), **3** (4-fluoro-3-nitroaniline), and **4** (*N*,*N*-dimethyl-4-fluoro-3-nitroaniline) (see Scheme 2) in a homogeneous aqueous solution.[14,15] Using the fluoroaromatics **5** or **6** for the substitution reaction in aqueous solution, partially insoluble PVAm fractions were obtained.[14] Those polymers are unsuitable to further applications.

The objective of this work is to show that the functionalization reaction can be directly carried out on the silica particle surface. The advance of this one-step reaction is that the functionalization of PVAm with chromophores and the consecutive adsorption of the modified PVAm on the silica surface take place simultaneously. Therefore, chemically induced subsequent cross-linkage can be avoided in the surrounding solution. The large specific surface area of the employed silica particles guaranteed a high amount of adsorbed polymer.[3,4] Furthermore, silica particles are suitable for the most surface sensitive techniques and other analytical methods, such as UV/vis spectroscopy, X-ray photoelectron spectroscopy (XPS), and electrokinetic measurements.

The degree of surface functionalization of the silica surface is determined by the amount of immobilized PVAm after the nucleophilic substitution reaction took place as well as the amount of chromophore introduced in the polymer backbone. The complete amount of PVAm and chromophores can be calculated from the quantitative elemental analysis (C, N) of the carefully extracted and dried functionalized silica particle. This measurement does not allow distinguishing between the portions of PVAm and generated chromophore. The average amount of chromophore at the

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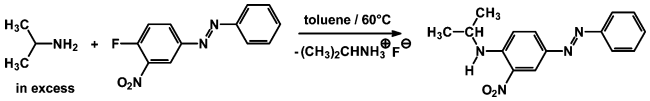
Scheme 3. Exemplary Synthesis of the Azo-Functionalized Model Compound (*N*-Isopropyl-4-azobenzene-2-nitroaniline) Used in These Studies



PVAm chains can be calculated from the redissolved fraction according to ref 14. UV/vis spectroscopy was used to identify the molecular structure of the main chromophoric fraction bonded to the polymer-coated silica in comparison to well-defined model compounds, which were synthesized from the corresponding fluoroaromatic compounds and isopropylamine according to ref 30 (see Scheme 3).

XPS was employed to study the chemical structure of the nitroaromatic derivatives incorporated into the PVAm chains. The reaction of the PVAm's with the nitroaromatic derivatives lowers the number of protonable amino groups.

Electrokinetic measurements were carried out in microelectrophoresis experiments to study the silica/polymer's charge behavior in aqueous solutions as a function of pH. Hence, shifts in the isoelectric points should give a hint on the amount of substituted primary amino groups.[3] Brunauer−Emmett−Teller (BET) measurements, elemental analyses, and particular solid state ^{13}C NMR spectroscopic investigations have been used to complete the analysis of the new materials.

Experimental Section

Materials. *Chemicals.* Aqueous solution samples of poly(vinylamine) (PVAm, 11.5 wt %, $M_n = 400\,000$ g mol^{-1}, pH =11, degree of hydrolysis = 97.3) were kindly provided by BASF AG (Ludwigshafen, Germany). PVAm was produced from the prepolymer poly(vinylformamide), where 97.3% of all formamide groups were converted into primary amino groups.

4-Fluoronitrobenzene (**1**, 4-FNB), 2-fluoronitrobenzene (**2**, 2-FNB), and 1-fluoro-2,4-dinitrobenzene (**5**, FDNB, Sanger's reagent) were purchased from Sigma-Aldrich Chemie GmbH (Seelze, Germany). 1,5-Difluoro-2,4-dinitrobenzene (**6**, DFDNB) and 4-fluoro-3-nitroaniline (**3**, 4-FNA) are commercially available products by Merck KGaA (Darmstadt, Germany) and ABCR GmbH (Karlsruhe, Germany). For purification, 4-FNB (**1**), 2-FNB (**2**), and Sanger's reagent (**5**) were distilled under reduced pressure. White crystals of DFDNB (**6**) were used without further purification. The brown powder of 4-FNA (**3**) was recrystallized from ethanol.

Silica. Silica (Kieselgel H) was purchased from Fluka (Sigma-Aldrich Chemie GmbH, Seelze, Germany). The chosen particle size of 5−40 μm was suitable for synthesis, spectroscopic measurements, and microelectrophoresis. More items of information on the silica are given below (see Table 3).

Syntheses of the Chromophoric, Nitrophenyl Functionalized PVAm− Silica Particles. For functionalization of silica with chromophoric groups and PVAm in water, 2.5 mmol of the fluoroaromate was dissolved in 30 mL of ethanol and suspended with 5 g of silica overnight. The solvent was removed by a rotary evaporator at 40 °C. Distilled water (30 mL) and 5.4 mL of aqueous solution of PVAm containing 0.5 g (8.3 mmol) of the polymer were added to the freshly prepared fluoroaromate-loaded silica particles. The mixture was refluxed for 12 h at 100 °C. After cooling to room temperature, the PVAm-functionalized silica was fritted off and washed carefully with water. Afterward, two Soxhlet extraction cycles, the first with water and the second with acetone, were carried out to remove nonbonded functionalized polymer and nonreacted fluoroaromate, respectively, from the silica particles' surface.

Synthesis of *N*,*N*-Dimethyl-4-fluoro-3-nitroaniline (4-DMFNA, 4). *N*,*N*-dimethyl-4-fluoro-3-nitroaniline (DMFNA) was synthesized via *N*,*N*-dimethylation of 4-fluoro-3-nitroaniline with formaldehyde/sodium borohydride in aqueous tetrahydrofuran according to Giumanini et al.[32] Red crystals with a melting point of 37−41 °C in 95% yield were obtained. ^{1}H NMR (300 MHz, δ, ppm, CD_2Cl_2): 7.21 (dd, 1*H*, $J = 5.49$ Hz, $J = 3.30$ Hz), 7.12 (dd, 1*H*, $J = 10.44$ Hz, $J = 9.34$ Hz), 6.90 (ddd, 1*H*, $J = 9.34$ Hz, $J = 3.85$ Hz, $J = 3.30$ Hz), 2.97 (s, 6*H*, $-N-(CH_3)_2$).

Synthesis of 4-Fluoro-3-nitroazobenzene (FNAzoB, 7). Condensation reaction of nitrosobenzene and 4-fluoro-3-nitrobenzene was performed in acetic acid according to Neunhoeffer and Ruske.[33] After recrystallization from ethanol, orange−yellow needles with a melting point of 134−135 °C in a yield of 65% were obtained. ^{1}H NMR (300 MHz, δ, ppm, d_6-acetone): 8.6 (dd, 1*H*, $J = 2.5$ Hz, $J = 7.05$ Hz), 8.37 (ddd, 1*H*, $J = 8.9$ Hz, $J = 4.2$ Hz, $J = 2.5$ Hz), 7.99 (m, 2*H*), 7.75 (dd, 1*H*, $J = 10.6$ Hz, $J = 8.9$ Hz), 7.62 ppm (m, 3*H*).

Synthesis of *N*-(2′,4′-dinitrophenyl)-4-fluoro-3-nitroaniline (*N*-DNP-FNA, 8). 4-Fluoro-3-nitroaniline (19.098 g, 0.1223 mol), 1-fluoro-2,4-dinitrobenzene (22.766 g, 0.1223 mol), and sodium hydrocarbonate (12.3463 g, 0.1470 mol) were stirred and heated for 2 h under reflux. The hot mixture was filtered off and gave the crude product during cooling. After several times of recrystallization from ethyl acetate, yellow crystals with a melting point of 186−188 °C in a yield of 40% were obtained. ^{1}H NMR (300 MHz, δ, ppm, d_6-acetone): 10.17 (s, 1*H*), 9.04 (d, 1*H*, $J = 2.7$ Hz), 8.29 (m, 2*H*, $J = 8.9$ Hz, $J = 9.3$ Hz), 7.96 (m, 1*H*, $J = 8.9$ Hz), 7.68 (dd, 1*H*, $J = 8.9$ Hz, $J = 11$ Hz), 7.39 (d, 1*H*, $J = 9.3$ Hz).

Synthesis of 4-fluoro-3,4′-dinitrostilbene (FDNstilbene, 9). The Horner−Wadsworth−Emmons reaction[34] of 4-fluoro-3-nitrobenzaldehyde (Aldrich) with 4-nitrobenzyl-diethyl-

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phosphonate (Acros) with sodium ethoxide in tetrahydrofuran was used. 4-Nitrobenzyldiethylphosphonate (3.23 g, 11.8 mmol) was dissolved in 50 mL of dry tetrahydrofuran (THF) and cooled to 0 °C. Sodium ethoxide (0.80 g, 11.8 mmol) in 50 mL of THF was added dropwise, and the solution was stirred for 30 min. Then a THF solution (50 mL) of 4-fluoro-3-nitrobenzaldehyde (2 g, 11.8 mmol) was slowly added dropwise and stirred at room temperature overnight. The reaction mixture was poured into 400 mL of water for hydrolysis. The yellow precipitate was filtered off, washed several times with ethanol, and dried under vacuum. The yellow−orange product was obtained as a powder in 44% yield with a melting point of 212−216 °C. ^{1}H NMR (400 MHz, δ, ppm, CD_2Cl_2): 8.24 (dd, 1*H*, J = 4.40 Hz, J = 2.56 Hz), 8.22 (d, 2*H*, J = 8.79 Hz), 7.82 (ddd, 1*H*, J = 8.79 Hz, J = 4.40 Hz, J = 2.56 Hz), 7.68 (d, 2*H*, J = 8.79 Hz), 7.35 (dd, 1*H*, J = 10.62 Hz, J = 8.79 Hz), 7.26 (d, 1*H*, J_{trans} = 16.48 Hz), 7.22 (d, 1*H*, J_{trans} = 16.48 Hz).

Determination of the Degree of Substitution of the Nitrophenyl Functionalized PVAm. The degree of substitution s was determined by a known method, using eq 1 if the molar absorption coefficient of a model compound and those of the functionalized PVAm are known from UV/vis-spectroscopic determination.[31]

$$s = \frac{\epsilon' M_{eq}}{\epsilon_{Model} - \epsilon' M_s} \quad (1)$$

In eq 1, s = degree of substitution (number of substituents per basic building block), ϵ' = molar absorption coefficient of the polymer (L g^{-1} cm^{-1}), M_{eq} = molecular weight of the basic building block (chromophoric unit), ϵ_{Model} = molar absorption coefficient of the model compound (L mol^{-1} cm^{-1}), and M_s = molecular weight of the incoming substituent (without fluorine). This calculation requires the presumption that the average amount of the redissolved fraction shows no difference to that of the immobilized fraction. UV/vis spectroscopic investigations support that the order of magnitude of PVAm functionalization of immobilized and redissolved polymer is similar.

Syntheses of the Nitroaniline Derivatives (Model Compounds). Synthesis of the model compounds *N*-isopropyl-4-nitroaniline, *N*-isopropyl-2-nitroaniline, *N*-isopropyl-2,4-dinitroaniline was accomplished by reaction of isopropylamine with the corresponding fluoronitroaromatics.[30] For synthesis and characterization of *N*,*N*′-diisopropyl-2,4-dinitrobenzene-1,5-diamine, see ref 14.

Synthesis of the Model Compound *N*-Isopropyl-4-azobenzene-2-nitroaniline. 4-Fluoro-3-nitroazobenzene (FNAzoB, 1.0 g, 4 mmol) was dissolved in 40 mL of toluene, and 1 mL of isopropylamine (24 mmol) was added. The reaction mixture was heated for 12 h at 80 °C. Then, the excess of isopropylamine and solvent were distilled off at 140 °C. The solid orange residue was recrystallized from methanol, giving intense orange needles with a melting point of 90−91 °C in 90% yield. ^{1}H NMR (300 MHz, δ, ppm, CD_2Cl_2): 8.77 (d, 1*H*, J = 2.20 Hz), 8.36 (s, 1*H*, −N*H*), 8.10 (dd, 1*H*, J = 9.34 Hz, J = 2.20 Hz), 7.86 (dd, 2*H*, J = 8.24 Hz, J = 1.65 Hz), 7.45−7.55 (m, 3*H*, J = 8.79 Hz, J = 8.24 Hz), 7.01 (d, 1*H*, J = 9.34 Hz), 3.96 (m, 1*H*, −C*H*−$(CH_3)_2$), 1.38 (d, 6*H*, −CH−(C*H*$_3)_2$).

Synthesis of the Model Compound *N*-Isopropyl-4-*N*-(2′,4′-dinitrophenyl)-2-nitro-*p*-phenylenediamine. *N*-(2′,4′-Dinitrophenyl)-4-fluoro-3-nitroaniline (*N*-DNP-FNA, 1.0 g, 3.1 mmol) was dissolved in 80 mL of toluene, and 1.3 mL of isopropylamine (15.5 mmol) was added. The reaction mixture was heated for 6.5 h at 80 °C. Then, the excess of isopropylamine and solvent were distilled off at 140 °C. The solid red residue was recrystallized from methanol, giving dark red crystals in 91% yield with a melting point of 147−149 °C. ^{1}H NMR (400 MHz, δ, ppm, CD_2Cl_2): 9.76 (s, 1H), 9.12 (d, 1*H*, J = 2.56 Hz), 8.16 (dd, 1*H*, J = 9.52 Hz, J = 2.56 Hz), 8.13 (d, 1*H*, J = 2.56 Hz), 8.09 (s, 1*H*, N*H*−CH−$(CH_3)_2$), 7.38 (dd, 1*H*, J = 9.16 Hz, J = 2.56 Hz), 7.02 (d, 1*H*, J = 9.16 Hz), 7.00 (d, 1*H*, J = 9.52 Hz), 3.90 (m, 1*H*, −C*H*−$(CH_3)_2$), 1.38 (d, 6*H*, −CH−(C*H*$_3)_2$).

Synthesis of the Model Compound 4-*N*-Isopropylamino-3,4′-dinitrostilbene. 4-Fluoro-3,4′-dinitrostilbene (FDNstilbene, 0.43 g, 1.5 mmol) was dissolved in 30 mL of toluene, and 0.64 mL of isopropylamine (7.5 mmol) was added. The reaction mixture was heated for 2 h at 60 °C. Then, the excess isopropylamine and solvent were distilled off at 140 °C. The solid orange residue was recrystallized from methanol to give orange−red crystals with a melting point of 167−169 °C in 47% yield. ^{1}H NMR (400 MHz, δ, ppm, d_6-acetone): 8.35 (d, 1*H*, J = 2.20 Hz), 8.23 (dd, 2*H*, J = 9.16 Hz, J = 2.20 Hz), 8.14 (d, 1*H*, −N*H*), 7.95 (dd, 1*H*, J = 9.16 Hz, J = 2.20 Hz), 7.85 (d, 2*H*, J = 9.16 Hz), 7.52 (d, 1*H*, J_{trans} = 16.48 Hz), 7.31 (d, 1*H*, J_{trans} = 16.48 Hz), 7.19 (d, 1*H*, J = 9.16 Hz), 4.05 (m, 1*H*, −C*H*−$(CH_3)_2$), 1.37 (d, 6*H*, −CH−(C*H*$_3)_2$).

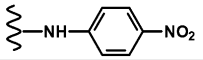
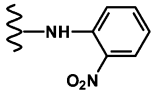
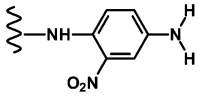
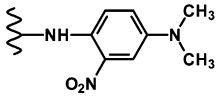
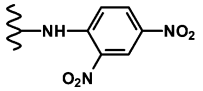
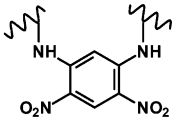
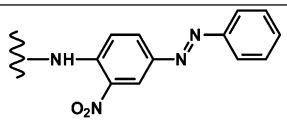
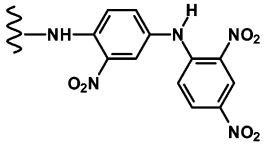
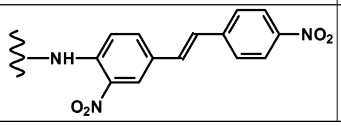
NMR Spectroscopic Measurements. The liquid NMR measurements were recorded at 20 °C on a Varian Gemini 400 FT NMR spectrometer, operating at 400 MHz for ^{1}H and at 100 MHz for ^{13}C. The signal of D_2O was used as the internal standard.

The solid-state ^{13}C{^{1}H}-CP-MAS NMR spectra were measured on a Bruker AMX 400 spectrometer. Chemical shifts were measured relative to adamantane.

UV/Vis Spectroscopic Measurements. UV/vis absorption spectra of functionalized PVAm/silica powder samples were measured employing a UV/vis MCS 400 diode-array spectrometer (Carl Zeiss) connected to a diffuse reflectance accessory via glass-fiber optics.

X-ray Photoelectron Spectroscopy (XPS) Measurements. The XPS studies were carried out with an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, U.K.). The spectrometer was equipped with a monochromatic Al Kα ($h\cdot\nu$ = 1486.6 eV) X-ray source of 300 W at 15 kV. The kinetic energy of the photoelectrons was determined with a hemispherical analyzer set to a pass energy of 160 eV for wide-scan spectra and 20 eV for high-resolution spectra. During all measurements, electrostatic charging of the sample was prevented with a low-energy electron source working in combination with a magnetic immersion lens. Later, the spectra were mathematically shifted by the value which was necessary to set the C 1s component peak of the saturated hydrocarbons to 285.00 eV.

Table 1. Degree of Substitution s of Various Chromophoric Poly(vinylamine)s onto Silica Particles by Using the Molar Absorption Coefficients of Model Compounds in Methanol via UV/Vis Spectroscopy [Initial Amount of n (fluoro compound)/*n* (PVAm)/n (silica) = 0.3:1:10]

	Fluoro compound used	Formed chromophoric unit of the PVAm on silica	ε_{Model} in methanol [$l\ mol^{-1}\ cm^{-1}$]	Degree of substitution s [mol%]
1	4-FNB		2.23×10^4 (390 nm)	7.0 (UV/vis)
2	2-FNB		5.95×10^3 (430 nm)	34.5 (UV/vis)
3	4-FNA		-	13.3 (^{1}H-NMR)
4	4-DMFNA		-	3.3 (^{1}H-NMR)
5	FDNB		7.19×10^3 (410 nm)	indeterminable
6	DFDNB		1.13×10^4 (417 nm)	indeterminable
7	FNAzoB		8.96×10^3 (440 nm)	indeterminable
8	4-N-DNP-FNA		1.52×10^4 (362 nm)	2.0 (UV/vis)
9	FDNstilbene		2.64×10^4 (389 nm)	17.5 (UV/vis)

Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. The background spectrum was subtracted according to Shirley.[35] The free parameters of the spectrum deconvolution into component peaks were the binding energy (BE), height, full width at half-maximum (fwhm), and the Gaussian−Lorentzian ratio. During all measurements, the base pressure in the anaylsis chamber was $<10^{-6}$ Pa.

Electrokinetic Measurements. All electrokinetic measurements were performed as electrophoresis experiments with a ZetaSizer 3 (Malvern, U.K.). The samples were suspended in 10^{-3} mol L^{-1} KCl solutions. The pH values were adjusted with 0.1mol L^{-1} HCl or 0.1 mol L^{-1} KOH, respectively. The particle velocities in an electrical field with a strength of 120 V cm^{-1} were measured by laser Doppler anemometry employing a He/Ne laser. The electrokinetic potential (zeta potential, ζ) values were calculated from the measured velocities according to the Smoluchowski's equation.[36]

Results and Discussion

The synthetic procedure for producing the chromophore-substituted poly(vinylamine) coated silica particles has been adjusted concerning the optimal time for reaction and choice of the polymer. We have used a full hydrolyzed PVAm with a degree of hydrolysis of about 97.3 wt %, because PVAm with a middle degree (20−80 wt %) of amino groups undergoes intramolecular amidinium ring formation upon treatment with an acid (silica), which is disturbing.

Commercially available PVAm with a molecular mass of about 400 000 g mol^{-1} adsorbs in a larger amount on silica compared to other available samples of lower molecular weight.[3] Therefore, we have chosen an aqueous solution of poly(vinylamine) with M_n = 400 000 g mol^{-1} and pH = 11 especially for this work.

Silica-free nitrophenyl-functionalized PVAm's show varying solubility behavior. While the PVAm treated with 4-FNB (**1**) and 2-FNB (**2**) is readily soluble in both water and methanol, the 2,4-dinitrophenyl-functionalized PVAm is only

(35) Shirley, D. A. *Phys. Rev. B* **1972**, *5*, 4709−4714.

(36) Nitzsche, R.; Simon, F. *tm−Technisches Messen: Sensoren, Geräte, Systeme* **1997**, *64*, 106−113.

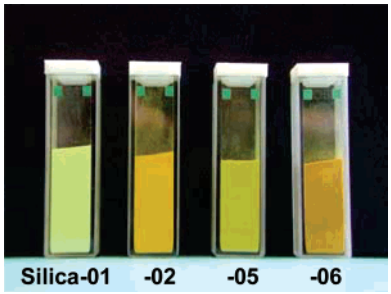


Figure 1. Photograph of functionalized PVAm/silica-01, -02, -05, and -06 (4-nitrophenyl-, 2-nitrophenyl-, 2,4-dinitrophenyl-, and 2,4-dinitro-1,5-phenylenediamine-functionalized PVAm onto silica particle).

partially soluble in water and methanol with swelling in the latter. The PVAm treated with DFDNB (**6**) is only sparingly soluble in water and insoluble in methanol. The PVAm treated with FNazoB (**7**) is insoluble in water and methanol. The solubility of PVAm treated with 4-FNA (**3**) and 4-DMFNA (**4**), respectively, was improved in water. Using the integral ratio of the aromatic protons at 7.0−7.5 ppm to the CH_2−CH protons of the polymer chain at 1.3−1.6 ppm (−CH_2 groups) and 2.8−3.1 ppm (−CH groups), the degree of substitution of the 2-nitro-1,4-benzenediamine-functionalized PVAm derivatives (polymer 3 and polymer 4) was determined by ^{1}H NMR spectroscopy in D_2O (see Table 1).

Model compounds were synthesized to determine the degree of substitution of the nitrophenyl-functionalized PVAm's by means of UV/vis spectroscopy (see eq 1).[14] The structure of the respective model compounds relates to the expected chromophoric unit in the polymer. Because the model compounds are insoluble in water, the molar absorption coefficients ϵ_{Model} were determined in methanol by UV/vis spectroscopy. PVAm treated with **5**, **6**, and **7**, respectively, was not completely soluble in water or methanol. Thus, the degree of substitution for these modified silica samples could not be determined using the procedure from eq 1. Conversion cannot be determined, since enhanced cross-linking reactions occur as observed for the high reactive fluoroaromatics **5**, **6**, and **7**, because the amount of extractable fraction is negligible and not representative for the immobilized one. An idea to circumvent the high reactivity problem was to use a lower reaction temperature (293 K). Unfortunately, this procedure is completely unsuitable, because a rapid precipitation of the functionalized polymer takes place associated with a gel process involving the silica particles. Then, it was not possible to separate the functionalized particles from the mixture. Therefore, all functionalization reactions have been carried out at 100 °C (373 K).

The quantitative results of the degree of substitution of the chromophoric poly(vinylamine)s onto silica particles and the molar absorption coefficients of the related model compounds in methanol are summarized in Table 1.

A series of functionalized silica particles produced by this methodology are shown in the photograph in Figure 1.

UV/vis absorption spectra have been recorded from the solid dried powders. As reference, a PVAm-functionalized silica was used, which was prepared by adsorption of PVAm on silica in water. The intense colored PVAm/silica-05, -06, -07, and -09 were mixed and ground with bare silica for

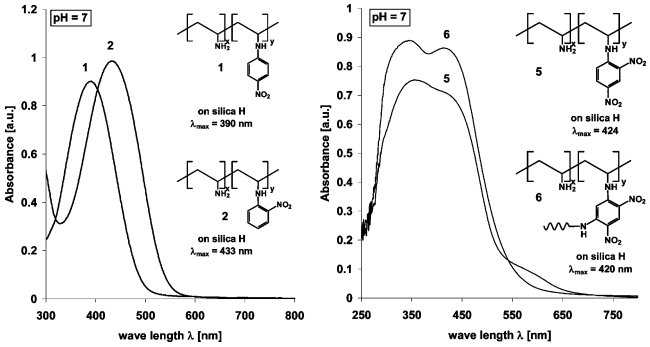


Figure 2. UV/vis absorption spectra of functionalized PVAm/silica-01, -02, -05, and -06 (4-nitrophenyl-, 2-nitrophenyl-, 2,4-dinitrophenyl-, and 2,4-dinitro-1,5-phenylenediamine-functionalized PVAm onto silica particles).

UV/vis spectroscopic measurements. The UV/vis absorption spectra of the silica-01, -02, -05, and -06 are shown in Figure 2.

As presumed, the incomplete solubility of the 2,4-dinitrophenyl-functionalized PVAm (reaction of Sanger's reagent with PVAm) in water is likely attributed to the fact that one of the two nitro groups is also substituted by an amino group derived from the PVAm. The concentration of those structure moieties is too low to be detectable by solid-state ^{13}C{^{1}H}-CP-MAS NMR- or DRIFT-spectroscopic investigations. The solid-state ^{13}C{^{1}H}-CP-MAS NMR spectrum shows only wide aromatic signals. An indication for the disubstitution reaction is the appearance of a shoulder in the UV/vis absorption spectrum of silica-05 at $\lambda = 550$ nm, which is not observed in the soluble fraction of 2,4-dinitrophenyl-functionalized PVAm in water (see Figure 2). This signal relates to silica-03 because an identical chromophore is present for which the UV/vis band position is pH-dependent. At pH = 1, the shoulder at 550 nm disappears on silica-05 according to ref 15, which is a strong hint at cross-linking that occurred by disubstitution. Thus, 2,4-dinitrophenyl-functionalized PVAm on silica (silica-05) behaves similarly to 2,4-dinitro-1,5-phenylenediamine-functionalized PVAm (silica-06).

The influence of pH on the UV/vis spectral properties was studied for all samples. No remarkable effects were observed for the chromophore-functionalized PVAm/silica-01, -02, -05, -06, -07, -08, and -09. The UV/vis absorption spectra of the samples silica-07, -08, and -09 are shown in Figure 3. The photographs of the functionalized silica-07, -08, and -09 are shown in the inset.

Silica-03 (2-nitrophenylenediamine-functionalized PVAm/silica) and silica-04 (*N*,*N*-dimethyl-3-nitro-*p*-phenylenediamine functionalized PVAm/silica), respectively, show a significant effect of the UV/vis absorption on pH (see Figure 4). In acidic medium (pH = 1), both samples are colored yellow (for silica-03, $\lambda_{max} = 420$ nm; for silica-04, $\lambda_{max} = 429$ nm**)**. In basic medium (pH = 11), both samples show a purple color (for silica-03, $\lambda_{max} = 512$ nm; for silica-04, $\lambda_{max} = 490$ nm).

The significant dependence of the UV/vis absorption wavelength of the silica particles on pH shows the analytical potential of the chromophore-functionalized particles as indicators to evaluate the proton concentration in solutions,

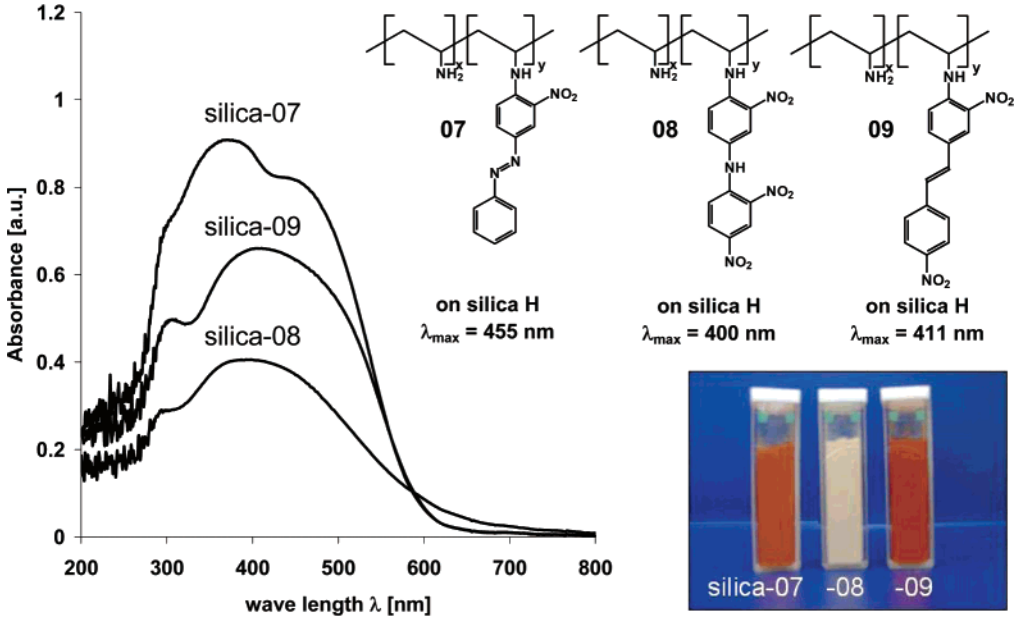


Figure 3. UV/vis absorption spectra of 4-azobenzene-2-nitrophenyl−(silica-07), 4-*N*-(2′,4′-dinitrobenzene)-2-nitrophenyl−(silica-08), and 4′-nitrostilbene-2-nitrophenyl−(silica-09) functionalized PVAm/silica particles (inset: photograph of functionalized PVAm/silica-07, -08, and -09).

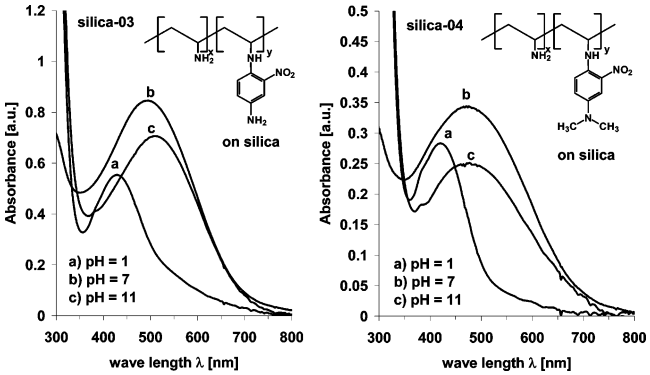


Figure 4. Influence of pH on the UV/vis absorption of 2-nitro-*p*-phenylenediamine-functionalized PVAm/silica (silica-03) and *N*,*N*-dimethyl-3-nitro-*p*-phenylenediamine-functionalized PVAm/silica (silica-04).

melts, or solids, especially particle-filled or fiber-enhanced composite materials as well as biomaterials.[15]

Table 2 shows the results of the quantitative elemental analyses (C, N) of the chromophoric silica particles. The overall degree of functionality relating to the gross amount of PVAm and fluoroaromate ranges between 15.2% (silica-08) and 82.5% (silica-06). As expected from the kinetic results from ref 14, the conversion clearly correlates with the reactivity of the fluoroaromatic.

XPS Spectroscopic Investigation. XPS spectra were taken from all chromophore PVAm-modified silica particles. Figure 5 shows wide-scan XPS spectra of unmodified silica (a), PVAm adsorbed onto silica (b), 2,4-dinitrophenyl-functionalized PVAm/silica (silica-05) (c), and 2,4-dinitro-1,5-phenylenediamine-functionalized PVAm/silica (silica-06) (d). The inset shows the regions of the F 1s spectra of the functionalized hybrid materials. Residual fluorine has been found in all samples.

In the case of functionalization with DFDNB, a more intensive F 1s peak is observed. The inset in Figure 5d shows that this F 1s peak is composed of two component peaks indicating two chemically different fluorine species. While the binding energy of component peak *G* agrees with the binding energy of the fluorine traces found in all other samples (BE ≈ 688.9 eV), component peak *H* shows a significantly lower binding energy (BE ≈ 686.6 eV), which is rather typical for the fluoride anion. A direct bond of fluorine to an electron-rich phenyl ring should decrease the F 1s binding energy. However, the relatively small amount of the detected fluorine species makes sure that both fluorine atoms of the DFDNB were substituted during the reaction with the PVAm molecule. (Quantitative elemental ratios were determined from the XPS analyses; see Supporting Information).

The high-resolution C 1s spectrum (Figure 6) shows that the majority of carbon is derived from the adsorbed PVAm. The spectrum was deconvoluted into three component peaks.

Table 2. Results of the Quantitative Elemental Analyses of the Surface Functionalization of Silica Using Various Fluoroaromatics with PVAm (initial amount of $n_{(\text{fluoro compound})}/n_{(\text{PVAm})}/n_{(\text{silica})} = 0.3{:}1{:}10$)'

fluoro compound used	silica sample	$C_{measured}$ (%)	$C_{calculated}$ (for complete conversion) (%)	ratio of $C_{measured}$ to $C_{calculated}$ (%)	$H_{measured}$ (%)	$N_{measured}$ (%)
none	silica-PVAm	2.62	3.74	70.05	1.1	1.14
4-FNB	silica-01	1.99	6.71	29.66	1.14	0.53
2-FNB	silica-02	2.17	6.71	32.34	1.12	0.68
4-FNA	silica-03	2.58	6.66	38.74	1.16	0.87
4-DMFNA	silica-04	2.51	7.62	32.94	1.21	0.78
FDNB	silica-05	5.12	6.58	77.81	1.35	2.22
DFDNB	silica-06	5.43	6.58	82.52	1.44	2.12
FNAzoB	silica-07	4.14	9.45	43.81	1.22	1.42
4-N-DNP-FNA	silica-08	1.39	9.15	15.19	1.09	0.50
FDNstilbene	silica-09	3.25	10.13	32.08	1.31	0.62

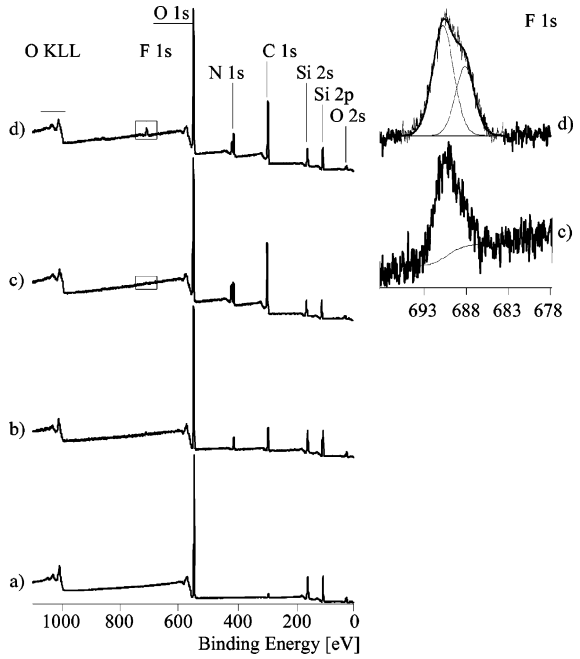


Figure 5. Wide-scan XPS spectra of unmodified silica (a), PVAm adsorbed onto silica (b), 2,4-dinitrophenyl-functionalized PVAm/silica (silica-05) (c), and 2,4-dinitro-1,5-phenylenediamine-functionalized PVAm/silica (silica-06) (d). The inset shows the regions of the F 1s spectra of the functionalized hybrid materials.

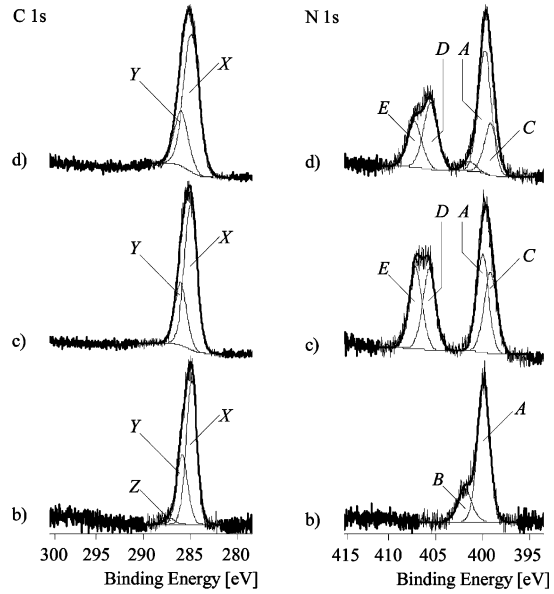


Figure 6. High-resolution C 1s and N 1s XPS spectra of PVAm adsorbed onto silica (b), 2,4-dinitrophenyl-functionalized PVAm/silica (silica-05) (c), and 2,4-dinitro-1,5-phenylenediamine-functionalized PVAm/silica (silica-06) (d).

The main component *X* shows saturated hydrocarbons (C_xH_y). The second component peak *Y* represents *C*—N amino bonds relating to the polyelectrolyte. The third component peak *Z* appears from the carbon of the nonhydrolyzed formamide groups in PVAm (O=*C*—NH). As can be seen in Figure 6, the high-resolution C 1s spectra do not show significant changes after the functionalization reactions with fluoroaromates. The formed secondary amines and the additionally introduced *C*—NO_2 groups cannot be separated from the component peak *Y*. The intensities of component peaks *Z* were too small to allow a trustworthy separation. Regarding the total amount of amino groups, the amount of formamide groups was determined to be ca. 8%, which is in good agreement with NMR data taken for the employed PVAm. According to the stoichiometry of PVAm, the area of component peak *X* should equal the area of component peak *Y*. Surface contaminations of hydrocarbons contribute to component peak *X* to double its intensity.

The corresponding N 1s spectrum (Figure 6) shows that primary amino groups (C—NH_2, component peak *A*) are equilibrated with protonated forms (C—N^+H_3, component peak *B*). The amide nitrogen also contributes to component peak *A*. The N 1s XPS spectra show two N 1s peak areas observed at about 400 and 406 eV for the samples using the fluoroaromatic **2**, **5**, **6**, **7**, and **9**, respectively. The signal at about 406 eV is not observed when the fluoroaromatic **1**, **3**, **4**, or **8** have been used. According to the literature, the signal at 406 eV is clearly attributable to the nitro group bonded at the phenyl ring.[37]

The nitro group causes a strong chemical shift of the N 1s signal to higher binding energies (Figure 6 parts c and d). According to the formal mesomerism, the two nitro groups should be chemically identical and appear as one component peak in the N 1s spectra. Surprisingly, all recorded N 1s of samples bearing a detectable number of nitro groups show a clear splitting of the C—NO_2 band into two component peaks indicated by *D* and *E*. The splitting of this signal at 406 eV into two signals at 405 and 407 eV can be explained by an intramolecular hydrogen bond formation including a neighboring amino or nitroaniline moiety due to the push—pull character of *ortho*- or *para*-nitroanilines. The oxygen of the nitro group in the ortho-position of the secondary amino group can interact with the acid hydrogen of the amino group via a hydrogen bond. The nitro group in para-position cannot be involved in such intramolecular interaction along a polymer backbone. Hence, the electron densities on the nitrogen atoms of the two nitro groups should be different, and a chemical shift is observed. Unfortunately, it was not possible to produce a sample that has a clearly detectable amount of nitro groups only in the *para*-position. Basically, XPS analyses of 2-nitrophenyl-functionalized PVAm's at surfaces require additional future work using model compounds and comparison with other spectroscopic methods such as ^{13}C NMR spectroscopy. But this is not the objective of this work.

Now, we will discuss the lack of the nitro group signal despite the occurrence of the significant UV/vis absorption of the nitroaniline moiety for the samples silica-01, silica-03, silica-04, and silica-08. It is remarkable that the fluoro-nitroaromates **1**, **3**, **4**, or **8** are less reactive compared to **2**, **5**, **6**, **7**, or **9**. In other words, the N 1s signal for aromatic nitro groups is only observable if highly reactive fluoro-aromatics have been used for the functionalization reaction.

This result requires a detailed explanation. The different success to analyze the nitro group by means of XPS could be dependant on the place where the substitution reaction occur. The particles have a more-or-less spherical shape. In this case, the actual information depth (ID) of the XPS

(37) Liu, Yi-Chun; McCreery, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 11254—11259.

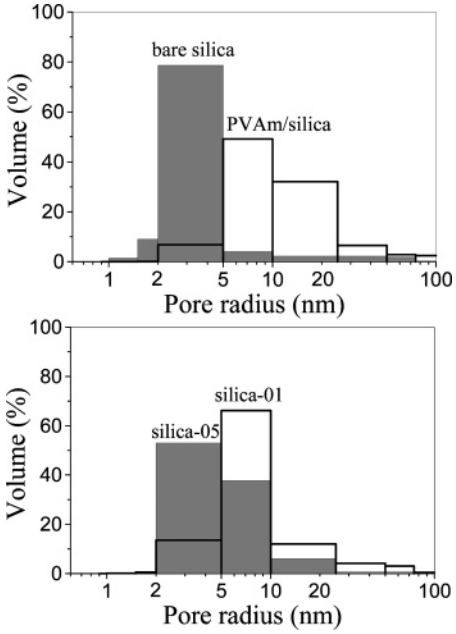


Figure 7. Pore-size distribution of bare silica, PVAm/silica, and chromophoric-functionalized PVAm/silica particles using differently reactive types of fluoroaromatics (silica-01 = 4-nitrophenyl-functionalized PVAm/silica and silica-05 = 2,4-dinitrophenyl-functionalized PVAm/silica).

methods follows an angular-dependent distribution where ID = ED(λ) cos θ. ED is the escape depth of photoelectrons depending on their mean free path λ, and θ is the angle between the sample's surface normal and the electron-optical axis of the XPS spectrometer.[38] The maximum escape depth for N 1s photoelectrons produced with Al Kα X-rays is not higher than 8 nm. But photoelectrons escaping the sample from this depth do not strongly contribute to the spectral information, because the angle θ changes with the curvature of the surface. Perhaps the electron beam cannot detect the nitro groups in the depth of the PVAm-loaded particles' surfaces? They are likely covered by a nonchromophore-functionalized PVAm. Therefore, it is assumed that the less-reactive fluoroaromatics have not reacted at the periphery of the PVAm-functionalized silica particles.

This interpretation is supported by the fact that samples showing the N 1s peak at 406 eV bear a low [Si]/[C] peak area intensity ratio in the XPS spectrum, excluding silica-02. But the intensity of the N 1s peak at 406 eV of silica-02 is much lower, as observed for the silica-05, -06, -07, and -09.

BET Analysis. An independent support for the hypothesis that the chromophores are differently located in the polymer layer provides the analysis of the pore-size geometry of the silica hybrid particles. The bare silica substrate used for the functionalization reaction shows a BET surface area of 395 $m^2\ g^{-1}$. The main average pore radius amounts to 5−10 nm. Figure 7 shows the pore-size distribution curves for bare silica, PVAm/silica, 4-nitrophenyl-functionalized PVAm/silica (silica-01), and 2,4-dinitrophenyl-functionalized PVAm/silica particles (silica-05). The results of the BET analyses of the functionalized samples are shown in Table 3.

Results of BET measurements and pore-size distribution strongly support the argument that aromatic nitro group

Table 3. BET Surface Area and Average Pore-Size Radius Range of the Various PVAm-Functionalized Silica Particles Compared with the C-Content Ratio from the Elemental Analysis

fluoro compound used	silica sample	BET ($m^2\ g^{-1}$)	average pore radius (%) 2−5 nm	average pore radius (%) 5−10 nm	ratio of $C_{measured}$ to $C_{calculated}$ (%)
none	bare silica	395	79	4	
none	PVAm/silica	143	7	49	70.05
4-N-DNP-FNA	silica-08	189	16	66	15.19
4-FNB	silica-01	181	14	66	29.66
FDNstilbene	silica-09	227	15	66	32.08
2-FNB	silica-02	227	24	60	32.34
4-DMFNA	silica-04	204	28	54	32.94
4-FNA	silica-03	191	18	64	38.74
FNAzoB	silica-07	193	56	36	43.81
FDNB	silica-05	274	53	38	77.81
DFDNB	silica-06	274	69	22	82.52

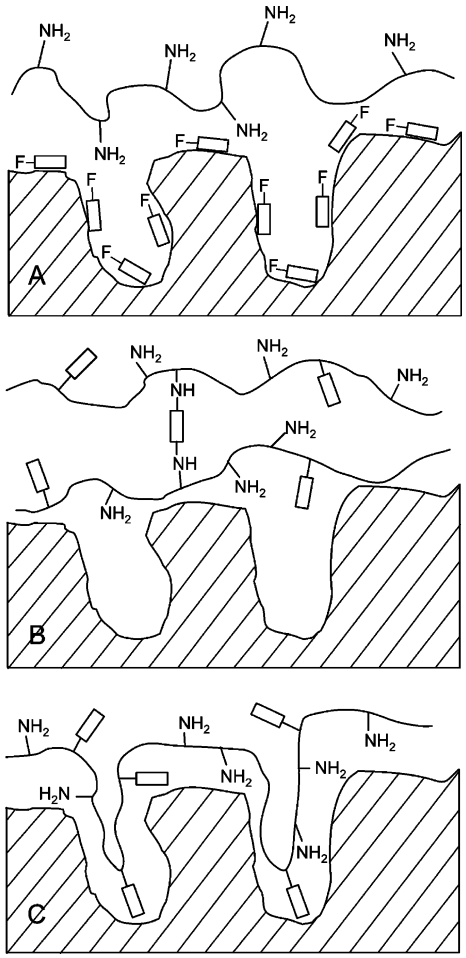
moieties are differently distributed in the PVAm layer. The vertical distribution seems to depend on the reactivity of the fluoroaromatic. Less-reactive fluoroaromatics such as 4-FNB (**1**), 4-FNA (**3**), and 4-DMFNA (**4**) preferably react with PVAm in the pores of silica, whereas more-reactive compounds rapidly react with the PVAm before they can enter the pores (see Scheme 4).

This explanation is supported by the fact that the adsorption of pure PVAm on silica results in a related pore-size distribution, just as when a lesser-reactive fluoroaromatic has been used. However, functionalization of PVAm with chromophores always disturbs the dense covering of the silica surface by PVAm. The effect is significantly observed for the micropores of 2−5 nm average pore radius when the highly reactive fluoroaromatics **5**, **6**, and **7** are used. Then, the pore-size distribution after functionalization comes closer to that of bare silica.

Electrokinetic Investigation. Electrokinetic measurements are established to study the charge distribution in an interphase, which is produced when a solid is in a thermodynamic equilibrium with a liquid. The employment of an aqueous solution as liquid phase offers the possibility to vary the pH of the surrounding of the solid and control the adsorption of hydronium ions (H_3O^+) and/or hydroxide ions (OH^-) on the solid surface. The inert salt (e.g., KCl) keeps the ion strength nearly constant during varying of the pH value. The correct execution of electrokinetic experiments, especially the microelectrophoresis and the correct transformation of the measured electrophoretic mobility into zeta-potential values, is controversially discussed in the literature.[3,4,36] The correct transformation of the measured values into zeta-potential values requires the knowledge of the permittivity and the viscosity of the liquid in the interphase and must consider the phenomenon of surface conductivity. This effect can be remarkable if high ion concentration differences in the double layer and the liquid, i.e., as a consequence of specific ion adsorption or dissociation of functional surface groups are present. However, in electrophoretic experiments, it seems not possible to determine such values with satisfactory precision. Hence, the zeta-potential values discussed here should be considered as apparent zeta-potential values. The pH-values were measured after adjustment of the thermodynamic equilibration between the solid and the liquid phase.

(38) Fadley, C. S. *Prog. Surf. Sci.* **1984**, *16*, 275−388.

Scheme 4. Suggested Model for the Reaction of Preadsorbed Fluoroaromatics with PVAm on the Silica Surface



(A, nitrobenzene derivative (rectangle) adsorbed onto silica before the reaction with PVAm starts; B, adsorption of functionalized PVAm through reaction of highly reactive fluoroaromatics with PVAm; C, adsorption of functionalized PVAm through reaction of less-reactive fluoroaromatics with PVAm).

Zeta-potential measurements show impressively the altering of the surface charge of the chromophoric-functionalized PVAm/silica particles compared to that of the bare silica. Figure 8 shows a series of zeta-potential values as function of the pH.

A strong shift of the isoelectric point (IEP) from pH = 2.5 of bare silica to pH $\approx$ 10 is observed for the silica samples silica-01, silica-02, silica-03, and silica-04. A weaker shift of the IEP to pH 8.4 $\leq$ 8.7 $\leq$ 9.0 is observed for the silica samples silica-05, silica-06, and silica-07. The IEP of functionalized pure PVAm/silica particles is located at pH = 9.8. The two groups of chromophore-functionalized PVAm/silica particles correlate well with the results of the BET measurements and XPS investigations. Since the empty pores are filled (less-reactive fluoroaromatics, Scheme 4C), a nearly complete surface coverage of the silanol groups is observed, as indicated by a stronger shift of the IEP, because the silanol groups are neutralized by the amino groups from

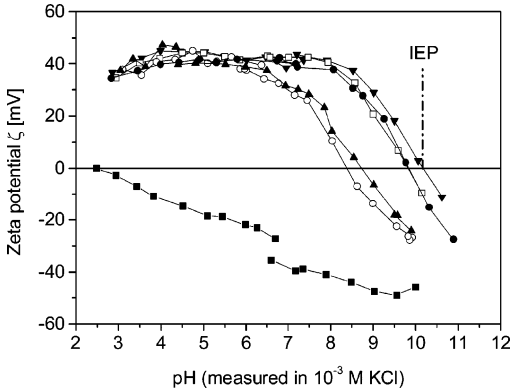


Figure 8. Dependence of the apparent zeta-potential values (ζ) on pH of an aqueous KCl solution ($c_{KCl} = 10^{-3}$ mol L^{-1}) determined from microelectrophoresis experiments. Bare silica (■), PVAm/silica (●), 4-nitrophenyl-functionalized PVAm/silica (▼ silica-01), 2-nitrophenyl-functionalized PVAm/silica (□ silica-02), 2,4-dinitrophenyl-functionalized PVAm/silica (○ silica-05), and 2,4-dinitro-1,5-phenylenediamine-functionalized PVAm/silica (▲ silica-06). The point indicated with IEP exemplarilyy shows the isoelectric point, which is the pH where the zeta potential is zero.

the PVAm layer. The IEP represents the equilibrium between free silanol groups and adsorbed amino groups. Therefore, free silanol groups on the silica surface are better accessible by hydroxide ions, since the polymer layer is stronger crosslinked and, thus, more rigid (highly reactive fluoroaromatics, Scheme 4B). Additionally, a larger part of amino groups are converted by the fluoroaromatic. Therefore, fewer amino groups are present to neutralize the silanol groups, and a weaker shift of the IEP results.

Conclusion

Preadsorption of reactive fluoroaromatics on silica and subsequent nucleophilic substitution with PVAm in water at 100 °C results in chromophoric-functionalized PVAm/silica particles. The PVAm−nitroaniline functionalities remain irreversibly fixed on silica, as shown by extraction experiments. The surface charge has been completely altered from a negative value of bare silica to a positive value of PVAm/silica, which shows that the functionalization process is very effective. By this new methodology, a lot of structurally different chromophores can be introduced. It is assumed that the vertical distribution of the chromophore is influenced by the reactivity of the fluoroaromatic used.

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Supporting Information Available: The supporting information includes a table that gives the quantitative XPS results for the relative element ratios of chromophoric-functionalized PVAm/silica particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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