Ultrathin Coatings by Multiple Polyelectrolyte Adsorption/Surface Activation (CoMPAS)

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ABSTRACT: A new versatile method for the preparation of thin polymer coatings is presented. It is based on the adsorption of reactive polyelectrolytes by electrostatic interactions. In a following activation step, the adsorbed polymers are modified by reacting with low molar mass reagents carrying the complementary charge, in order to induce charge reversal on the surface. This process allows regular layer-by-layer growth. Using coupling reactions that destroy or create dyes, in particular with donor−acceptor substitution, the multilayer growth can be easily followed. Coupling of azo dyes, aldol condensations of cyanine dyes and analogues, or Michael addition of reactive dyes was found to be particularly useful. The resulting multilayers inherently have a noncentrosymmetric structure.

The design of ultrathin polymer films by self-organization methods is continuously advancing in recent years.[1,2] Currently, such films are prepared by the Langmuir−Blodgett (LB) technique,[2,3] the chemical self-assembly method applying stepwise chemisorption of low molecular weight compounds followed by surface activation,[1,4] and the alternating physisorption of oppositely charged polyelectrolytes.[2,5−7]

Exploiting the self-organization of amphiphiles by the hydrophobic effect, the LB technique allows the fabrication of films down to 1 nm thickness which consist of well-defined inverse bilayers. Characteristically, the self-organization of the amphiphiles into individual monolayers at the air−water interface is completely decoupled from the layer buildup. The latter is achieved by dipping the substrate through the prefabricated monolayer. Within the individual monolayers, the molecular fragments are oriented relative to the support, thus exposing defined chemical groups at the surface. Although LB films are normally centrosymmetric due to the bilayer substructure, noncentrosymmetric structures can be realized by special, though demanding, procedures. The normally very poor stability of LB films has been considerably improved by the use of polymers in recent years.[8−11] Still, the LB technique requires expensive equipment and does not convene for nonplanar supports, automation, and large-scale applications. This has precluded technical applications so far, though the method is excellently suited for model studies.

Stepwise chemisorption results in coatings down to 1 nm. Layer cohesion is inherently good due to covalent or ionic bonding or somewhat weaker due to complexation. Monomolecular sublayers are formed in which the molecular fragments are aligned. Thus, the surfaces are chemically well defined, and noncentrosymmetry is easily achieved.[12−14] There is no obvious inherent restriction concerning nonplanar supports, automation, and large-scale applications. However, the method has been limited to a very small number of well-performing systems.[1] Crucially, it requires quantitative activation of the surfaces to yield high-quality coatings and to maintain multilayer growth.[14] Up to now, this problem has not been resolved satisfactorily.

Alternating physisorption of oppositely charged polyions is the most recent of the three “classical” methods.[5] The technique requires the use of two complementary materials, providing basically centrosymmetric coatings with good cohesion. As for chemical self-assembly, there seems to be no inherent restriction concerning nonplanar supports, automation, and large-scale applications. Also, the chemical structure of polyelectrolytes is extremely versatile. But compared to the two other techniques, the sublayer structure is less defined:[15] Bragg peaks for example are found only in exceptional cases.[16,17] There is virtually no alignment, let alone orientation of molecular fragments on the molecular level (for exceptions see refs 18−21). Thus, the chemical nature of the surfaces of such coatings is rather ill-defined.

In summary, all of the classical techniques are characterized by particular advantages and by particular limitations. Within this context, we have explored a new technique to prepare thin polymeric coatings that allows for the preparation of noncentrosymmetrical structures. The method is based on the adsorption of polymers combined with repeated surface activation, as sketched in Figure 1.[22,23] CoMPAS requires the use of hydrophobized ionic polymers carrying reactive groups. These polymers are adsorbed onto an oppositely charged support. Chemical activation of the reactive groups recreates an oppositely charged surface to which the reactive ionic polymer can bind again. Repeated adsorption−activation cycles thus yield multilayers of the desired thickness. The method does not require special equipment, and there is no obvious limitation concerning the shape and the size of the support.

The CoMPAS method exploits many of the individual strong points of the classical three methods, while avoiding some of their disadvantages. The method employs electrostatic interactions, the concept of surface activation, hydrophobic interactions, and the use of polymeric adsorbates. Electrostatic interactions are easy to realize and will result in strong bonding. Surface activation will inherently create noncentrosymmetry.

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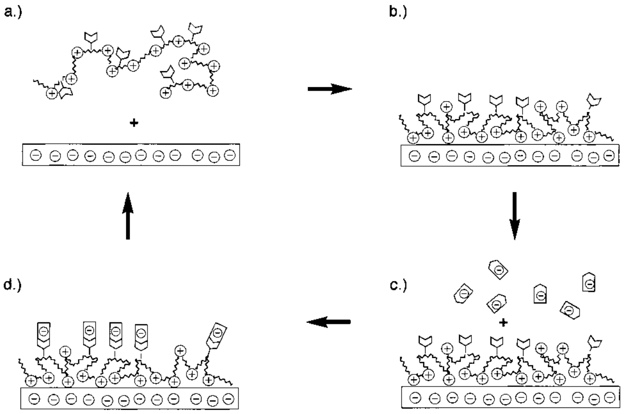


Figure 1. Scheme of the CoMPAS technique. (a) Physisorption step: a support having a negatively charged surface is dipped into the solution of a polycation containing reactive groups. (b) Adsorption of the polycation: reactive groups are presented at the surface. (c) Activation step: the assembly is dipped into a solution of a negatively charged molar mass reagent. (d) After the interfacial reaction, the negative surface charge is restored and the sample is ready for the next cycle

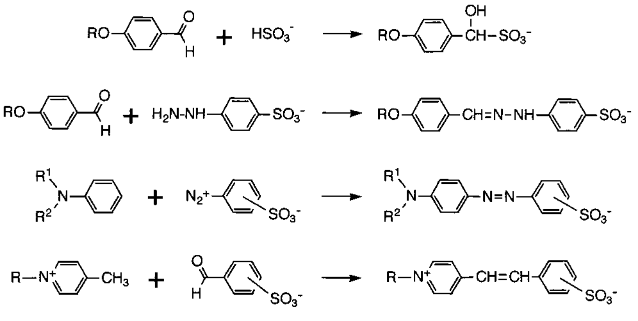


Figure 2. Reactions employed for the activation of polycations. From top to bottom: addition of $\mathrm{HSO_3^-}$ onto benzaldehydes, coupling of aldehydes with sulfonated phenylhydrazines, coupling of sulfonated diazonium salts with tertiary anilines, and condensation of 4-methylpyridinium salts with sulfonated aldehydes.

Hydrophobic interactions shall facilitate the accumulation of the reactive groups at the surface. The polymeric character of the adsorbates is essential to allow for an incomplete activation reaction, while simultaneously improving the stability of the coating.

As most substrates show negatively charged surfaces, we have focused for CoMPAS so far on reactive polycations. In this case, the activation reaction must introduce negatively charged groups into the adsorbed polymers. Numerous reactions seeming appropriate, we selected those that we thought to take place rather rapidly; i.e., reaction times are below 1 h. Also, reactions were chosen that are easily followed by UV/vis spectroscopy. This implies that the activation reaction is linked either to the formation or to the destruction of a strong chromophore. For this purpose, we chose the addition of bisulfite onto *p*-alkoxybenzaldehyde, the formation of phenylhydrazones, the azo coupling onto tertiary anilines, and the condensation of 4-methylpyridinium salts with aldehydes (Figure 2).

Experimental Section

Materials. All solvents were distilled prior to use and dried by standard procedures. Ethanol is dried and distilled over activated magnesium. Water was first deionized and then passed through a water purification system (ELGASTAT Maxima, 18 MOhm resistance). Flash chromatography was performed on silica gel (0.040−0.063 mm) and on neutral $\mathrm{Al_2O_3}$ (activity 1, ACROS).

Pure 4-chloromethylstyrene was purchased from ACROS. Reactive Black 5 (dye **32**), 3-(dimethylamino)propylmethacrylamide, branched poly(ethyleneimine), and poly(vinyl sulfate) were purchased from Aldrich. Potassium sulfopropyl methacrylate was a gift from Raschig AG (Ludwigshafen). 2,2′-Dimethyl-2,2′-azo-*N*-phenylpropionamidinium hydrochloride (VA545) and 2,2′-dimethyl-2,2′-azo-*N*-benzylpropionamidinium hydrochloride (VA552) were gifts from WAKO. Polyvinylamine was a gift from BASF. The syntheses of *N*-(11-methacryloyloxyundecyl)-4-methylpyridinium bromide (**17**), of poly(sulfopropyl methacrylate), and of polymers **7**, **11,** and **13** are described elsewhere.[24,25]

Synthesis of N-(2-Methacryloyloxyethyl)-N,*N*-dimethyl-*N*-12-(4′-formylphenyloxy)dodecylammonium bromide, **1.** 4-(12′-Bromododecyloxy)benzaldehyde is prepared from 1,12-dibromododecane and 4-hydroxybenzaldehyde analogously to compound **2**. Purification by flash chromatographie (eluent: petrol ether/ethyl acetate, 20 v/1 v) gives a colorless, waxy solid in 34% yield (a major side product is the colorless, waxy bis(1,12-(4′-formylphenyloxy)dodecane). 1.0 g of 4-(12-bromododecyloxy)benzaldehyde (2.7 mmol), 1.72 g of 2-(dimethylamino)ethyl methacrylate (10.8 mmol), and a few milligrams of inhibitor 2,6-di-*tert*-butyl-4-methylphenol are stirred in 40 mL of dry ethyl acetate at 60 °C for 9 days. On cooling, a colorless solid precipitates. The precipitate was washed with diethyl ether, repeatedly recrystallized from ethyl acetate, and dried in vacuo, yielding 0.76 g (53%) of colorless, hygroscopic solid.

^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, δ in ppm): 1.1−1.5m (16H, $-(\mathrm{CH_2})_8-$), 1.65−1.85m (4H, $-\mathrm{N^+C{-}CH_2}-$, $-\mathrm{CH_2{-}C{-}O}-$), 1.95s (3H, $=\mathrm{C{-}CH_3}$), 3.45s (6H, $\mathrm{N^+CH_3}$), 3.6m (2H, $\mathrm{N^+{-}CH_2}-$), 4.05t (2H, $-\mathrm{CH_2{-}O}-$), 4.15m (2H, $-\mathrm{COO{-}C{-}CH_2{-}N^+}$), 4.65m (2H, $-\mathrm{COO{-}CH_2}-$), 5.65s and 6.15s (2H, $\mathrm{CH_2}=$), 6.95d and 7.80d (2H + 2H, aryl), 9.85s (1H, −CHO)

^{13}C NMR ($\mathrm{CDCl_3}$, δ in ppm): 18.3 ($-\mathrm{CH_3}$), 22.9 ($\mathrm{N^+{-}C{-}}C\mathrm{H_2}-$), 25.9 ($\mathrm{N^+{-}C{-}C{-}}C\mathrm{H_2}-$), 26.2 ($-C\mathrm{H_2{-}C{-}O{-}aryl}$), 29.0 ($\mathrm{C_7}$ alkyl chain), 51.9 ($\mathrm{N^+CH_3}$), 58.1 ($-\mathrm{CH_2{-}O{-}aryl}$), 62.2 ($\mathrm{N^+{-}CH_2}-$), 65.5 ($-\mathrm{COO{-}C{-}}C\mathrm{H_2{-}N^+}$), 68.4 ($-\mathrm{COO{-}CH_2}-$), 114.0 ($-\mathrm{C_{aryl}}$, o-position of ether), 127.5 ($\mathrm{CH_2}=$), 129.7 ($-C_\mathrm{aryl}-\mathrm{CHO}$), 132.0 ($-\mathrm{C_{aryl}}$, o-position of aldehyde), 135.2 ($=C-\mathrm{COO}$), 164.0 ($-\mathrm{C_{aryl}{-}O}-$), 166.4 (−COO−), 191.0 (−CHO).

Microanalysis: Calcd for $\mathrm{C_{27}H_{44}BrNO_4{\cdot}H_2O}$ ($M_\mathrm{r} = 526.57 + 18.02$): 59.55% C, 8.51% H, 2.57% N. Found: 59.62% C, 8.01% H, 2.65% N.

Attempted Polymerization of ***1.*** Homo- and copolymerizations of **1** with various amounts of *N*-(2-methacryloyloxyethyl)-*N*,*N*,*N*-trimethylammonium bromide were attempted in 10−20 wt % solutions in ethanol using initiator AIBN for 24 h at 60 °C, as well as in water using 2 mol % initiator VA545. No polymer could be isolated in any case.

Synthesis of Polymer ***4.*** 12.1 g of 1,4-dibromobutene (57 mmol, Aldrich) is refluxed with 12 g of anhydrous $\mathrm{K_2CO_3}$ and 10 mg of KI in 50 mL of dry acetone. 4.6 g (38 mmol) of 4-hydroxybenzaldehyde in 25 mL of acetone is added dropwise. After 15 h, the mixture is filtered hot, and the filtrate is evaporated. The solution of the residue in $\mathrm{CH_2Cl_2}$ is extracted with saturated aqueous $\mathrm{K_2CO_3}$ and water, dried over $\mathrm{MgSO_4}$, and evaporated. Purification by double flash chromatography (eluents petrol ether/ethyl acetate 10v:1v and $\mathrm{CH_2Cl_2}$), yielding 3.5 g (36%) of solid 4-(4′-bromobut-2-enyloxy)benzaldehyde, **2**.

^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, δ in ppm): 3.99d (2H, $-\mathrm{CH_2}$-Br), 4.61d (2H, $-\mathrm{O{-}CH_2}-$), 6.00−6.20m (1H, $=\mathrm{CH{-}C{-}Br}$), 6.25−6.40m (1H, $\mathrm{O{-}C{-}CH}=$), 7.00d and 7.79d (2H + 2H, aryl), 9.87s (1H, −CHO).

4.43 g (26.3 mmol) of hexamethylene diisocyanate is reacted with 3.07 g (25.8 mmol) of *N*-methyldiethanolamine in chlorobenzene.[26] The precipitate formed upon cooling is isolated and washed with acetone. The crude polymer is redissolved in *m*-cresol, reprecipitated into acetone, and dried in vacuo at 60 °C, to yield 5.2 g of polyurethane, **3**.

Microanalysis: Calcd ($[\mathrm{C_{13}H_{25}N_3O_4}]_n$, $M_\mathrm{r} = [287.34]_n$): 54.34% C, 8.77% H, 14.61% N. Found: 53.89% C, 8.00% H, 14.57% N.

^{1}H NMR (200 MHz, d_6-DMSO, δ in ppm): 1.20−1.30m (4H, $-\mathrm{CON{-}C{-}C{-}CH_2}-$), 1.35−1.50m (4H, $\mathrm{N{-}C{-}CH_2}-$), 2.20

(3H, NCH_3), 2.50−2.60 ($-CH_2N\langle$ + solvent), 2.80−3.00 (4H, $-CON-CH_2-$), 3.90−4.05m (4H, $-O-CH_2$), 7.00−7.15m (2H, $-NH-$).

1.80 g (7.00 mmol) of **2** and 2.00 g (7.00 mmol) of polyurethane **3** are stirred in 60 mL of DMF at 65 °C under argon for 3 days. The polymer is precipitated into ethyl acetate, filtered off, washed extensively, and dried at 60 °C in vacuo, to yield 2.85 g (75%) of **4** as hygroscopic solid. The polymer is soluble in trifluoroethanol, DMSO, and DMSO/water mixtures but insoluble in pure water and $CHCl_3$.

Microanalysis: Calcd for the fully quaternized polymer ($[C_{24}H_{36}BrN_3O_6]_n$, $M_r = [542.47]_n$): 53.13% C, 6.69% H, 7.74% N, 14.73% Br. Found: 50.38% C, 6.94% H, 7.43% N, 15.06% Br.

^1H NMR (200 MHz, d_6-DMSO, δ in ppm): 1.20−1.30 (4H, $CON-C-C-CH_2-$), 1.35−1.50 (4H, $CON-C-CH_2-$), 2.80−3.05 (4H, $CON-CH_2-$), 3.10 (3H, N^+CH_3), 3.60−3.75 (4H, $O-C-CH_2N^+$), 4.15−4.25 (4H, $=C-CH_2-N^+$), 4.35−4.50 (4H, $-COO-CH_2-$), 4.80−4.90 (2H, $-CH_2-O-$aryl), 5.95−6.20 (1H, $=CH-C-N^+$), 6.25−6.50 (1H, $=CH-C-O-$aryl), 7.15−7.25 (2H, CH aryl), 7.35−7.45 (2H, $-NH-$), 7.90−8.00 (2H, CH aryl), 9.85 (1H, $-CHO$).

FT-IR (KBr, selected bands in cm^{-1}): 3332 (s, NH, n); 2935, 2857 (s,CH_2, ν); 1715 (s, amide I), 1600 (s, C=C, ν); 1535 (s, amide II); 1460 (m, CH_2 δ), 1250 (s,C−N, ν); 1160 (s−m, C−O, ν).

Microanalysis, NMR, and IR spectra (no detectable band at 2800 cm^{-1}) indicate quantitative quaternization of the tertiary amine moieties of precursor **3**.

Synthesis of Polymers ***8.*** Solid 4-(4′-bromomethylbenzyloxy)-benzaldehyde (**5**) is prepared from 1,4-bis(bromomethyl)-benzene and *p*-hydroxybenzaldehyde in analogy to **2** and purified by double flash chromatography (silica gel, eluents: CH_2Cl_2 and CH_2Cl_2/petrol ether) 1v/1v); yield 43%.

^1H NMR (200 MHz, $CDCl_3$, δ in ppm): 4.49s (2H, $-CH_2$-Br), 5.13s (2H, $-O-CH_2-$), 7.06d (2H, CH aryl, o-position of ether), 7.40m (4H, CH aryl), 7.82d (2H, CH aryl, o-position of aldehyde), 9.88s (1H, $-CHO$).

0.50 g (2.9 mmol) of polymer **7** in 20 mL of ethanol p.a. is mixed with 0.90 g (2.9 mmol) of **5** at 60 °C, resulting in a colorless precipitate. After stirring the mixture for 2 h at 70 °C, the solvent is distilled off. The residue is dissolved in chloroform, precipitated into THF, and dried. Reprecipitation into THF from a solution in 2,2,2-trifluoroethanol/chloroform (1v/1v) and drying in vacuo yields 1.1 g (78%) of **8**. The polymer is soluble in DMF, DMSO, trifluoroacetic acid, and 2,2,2-trifluoroethanol but insoluble in water, methanol, ethanol, and chloroform.

^1H NMR (200 MHz, d_6-DMSO, δ in ppm): 0.7−1.25 ($-CH_3$ backbone), 1.4−2.1 ($-CH_2-$ backbone + $CON-C-CH_2-$, 3.05 (N^+CH_3), 3.1−3.5 ($-CON-CH_2-$ + $-CH_2-N^+$ + water), 4.75 (N^+-CH_2-aryl), 5.2 (aryl$-CH_2-O-$), 7.0−7.9 (CH aryl), 9.85s ($-CHO$).

Synthesis of Polymer ***9.*** The mixture of 1.5 g (5.1 mmol) of 4-(11-hydroxyundecyloxy)benzaldehyde, 1.2 g (5.6 mmol) of 4-bromomethylbenzoic acid, and 10 mg of 4-(dimethylamino)-pyridine in a 1v:1v CH_2Cl_2/DMF is cooled to 0 °C. 1.2 g (5.8 mmol) of *N,N*′-dicyclohexylcarbodiimide in 5 mL of CH_2Cl_2 is slowly added. The mixture is allowed to reach ambient temperature and is stirred for another 24 h. After filtration to remove the precipitated urea, the filtrate is evaporated. Flash chromatography (silica gel, eluent CH_2Cl_2) yields 0.35 g (14%) of colorless, solid 4-(11′-(4″-formylphenoxy)undecyloxycarbonylbenzyl bromide, **6**.

^1H NMR (200 MHz, $CDCl_3$, δ in ppm): 1.10−1.50m (14H, $-(CH_2)_7-$), 1.60−1.90m (4H, aryl$-O-C-CH_2-$ + $-CH_2-C-OOC$), 4.00t (2H, aryl$-O-CH_2-$), 4.30t (2H, $-CH_2OOC-$), 4.45s (2H, CH_2Br), 7.00d (2H, CH aryl, o-position of ether), 7.45d (2H, CH aryl), 7.80d (2H, CH aryl, o-position of aldehyde), 8.00d (2H, CH aryl, o-position of ester), 9.87s (1H, $-CHO$). 0.15 g (0.3 mmol) of **6** and 0.26 g (1.5 mmol of repeat unit) of polymer **7** are stirred in 10 mL of dry DMF at 60 °C for 24 h. Thin-layer chromatography indicates the consumption of **6**. Then, 0.23 g (1.8 mmol) of dimethyl sulfate is added, and the mixture is reacted at 60 °C for another 24 h. The solvent is mostly removed, the residuous oil is diluted by $CHCl_3$, and the polymer is precipitated into THF. Lyophilization from water gives 0.22 g of **9** as colorless, hygroscopic powder. The polymer is soluble in DMF, DMSO, and water but insoluble in methanol, chloroform, and THF.

Microanalysis: 46.28% C, 7.89% H, 7.35% N, 3.34% Br, 7.67% S.

^1H NMR (200 MHz, D_2O, δ in ppm): 0.7−1.25 ($-(CH_2)_7-$ + $-CH_3$ backbone), 1.25−1.7 (aryl$-O-C-CH_2-$ + $-CH_2-C-OOC$ + $-CH_2-$ backbone), 1.9 ($CON-C-CH_2-$), 2.65 ($\rangle N-CH_3$ protonated), 3.10 (N^+CH_3 and $\rangle N-CH_2$ protonated), 3.30 ($-CH_2-N^+$ + $-CON-CH_2-$), 3.65s (CH_3OSO_3), 3.95 (aryl$-O-CH_2-$), 4.20 ($-CH_2OOC-$), 6.75 and 7.4−8.0 (CH aryl), 9.55 ($-CHO$). The signal of the N^+-CH_2-aryl group is superposed by the signal of the HDO.

FT-IR (KBr, selected bands in cm^{-1}): 3380 (s, NH ν); 2930, 2850, (s,$-CH_2$ ν); 1720 (m, $-C=O$, ν), 1646 (s, amide I); 1604 (w, C=C ν); 1534 (s, amide II), 1482 (m, $-CH_2$, δ); 1223 (s, $-OSO_3^-$ ν).

From the ratio of S and Br contents of the microanalysis, the copolymer composition is calculated as $x = 0.15$, $y = 0.82$, $z = 0.03$. From the intergretation of the NMR signals at 2.65, 3.65, and 6.5−8 ppm, the copolymer composition is calculated as $x = 0.15$, $y = 0.80$, $z = 0.05$.

Synthesis of Polymer ***10.*** 2.50 g (13.8 mmol) of *N*-phenyldiethanolamine, 4.80 g (28.7 mmol) of 4-bromobutyric acid, and 50 mg of 4-(dimethylamino)pyridine in 20 mL of CH_2Cl_2 are cooled to 0 °C. 6.60 g (32.0 mmol) of dicyclohexyl carbodiimide in 10 mL of CH_2Cl_2 is added dropwise. The mixture is stirred for 2 h at 0 °C and then for 24 h at ambient temperature. The precipitate of dicyclohexylurea is filtered off. The CH_2Cl_2 solution is extracted with saturated aqueous $NaHCO_3$ (Lösung), dried over $MgSO_4$, and evaporated. Purification by flash chromatography (eluent CH_2Cl_2/petrol ether 4v/1v) to yield 3.37 g (51%) of colorless, oily *N,N*-bis-(2-(4′-bromobutanoyloxy)-ethyl)aniline. ^1H NMR (200 MHz, $CDCl_3$, δ in ppm): 2.14m (4H, $-CH_2-C-Br$), 2.49t (4H, $-OOCCH_2-$), 3.44t (4H, $-CH_2$-Br), 3.63t (4H, $N-CH_2-$), 4.26t (4H, $-CH_2-OOC-$), 6.75m (3H, CH aryl, o-and p-position), 7.23t (2H, CH aryl, m-position). 2.09 g (4.17 mmol) of *N,N*-bis-(2-(4-bromobutanoyl)-oxyethyl)aniline and 0.54 g (4.17 mmol) of *N,N,N*′*,N*′-tetramethyl-1,3-propanediamine are stirred in 8 mL of DMF at ambient temperature under argon for 3 weeks. The polymer is precipitated into acetone, dried, redissolved in methanol, and reprecipitated into ethyl acetate. Lyophilization of the residue from water yields 1.92 g (73%) of slightly yellowish, hygroscopic polymer **10**.

Microanalysis ($[C_{25}H_{43}Br_2N_3O_4]_n$, $M_r = [609.23]_n$): Calcd: 49.27% C, 7.11% H, 6.89% N, 26.21% Br. Found: 46.38% C, 7.01% H, 6.17% N, 26.05% Br.

^1H NMR (200 MHz, D_2O, δ in ppm): 1.85 (4H, $N^+-C-CH_2-C-COO$), 2.20 (2H, $N^+-C-CH_2-C-N^+$), 2.35 (4H, $-OOCCH_2-$), 3.05 (12H, N^+CH_3), 3.15 and 3.30 (4H + 4H, $-CH_2-N^+-CH_2-$), 3.60 (4H, aryl-$N-CH_2$-), 4.25 (4H, $-CH_2-OOC-$), 6.4−7.0 (3H, CH aryl, o-and p-position), 7.25 (2H, CH aryl, m-position).

^{13}C NMR (50 MHz, d_6-DMSO, δ in ppm): 16.93 ($N^+C-\mathit{C}H_2-C-N^+$), 17.63 ($OOC-C-\mathit{C}H_2-C-N^+$), 30.10 ($OOC-\mathit{C}H_2-$), 48.80 ($N-\mathit{C}H_2-$), 50.54 ($N^+-CH_3$), 59.58 ($N^+\mathit{C}H_2-C-\mathit{C}H_2-N^+$), 61.54 ($-\mathit{C}H_2-OOC$), 62.72 ($OOC-C-C-\mathit{C}H_2-N^+$), 112.0 (aryl C_2), 116.3 (aryl C_4), 129.4 (aryl C_3), 147.4 (aryl, C_1), 172.2 ($-COO-$).

Synthesis of Copolymer ***12.*** 0.79 g (4.6 mmol) of 3-(dimethyl-amino)propylmethacrylamide and 1.00 g (4.6 mmol) of *N*-acryloyl-*N*′-phenylpiperazine[27] in 20 mL of ethanol are repeatedly degassed by freeze−thawing cycles and are polymerized for 20 h at 60 °C using 15.2 mg of AIBN as initiator. The polymer is precipitated into petrol ether and separated by centrifugation. This precursor copolymer is redissolved in 10 mL of dry THF. The mixture is reacted with 2.9 mL of bromoethane at 40 °C for 72 h and precipitated into petrol ether, and the polymer is isolated and dried. Yield: 1.43 of lightly brownish, very hygroscopic solid.

^1H NMR (200 MHz, D_2O, δ in ppm): 0.8−2.3 ($-CH_3$ backbone + $-CH_2-$ backbone + $-CH_2-C-N^+-C-CH_3$ +

−CH−CON⟨ backbone), 2.8−4.1 (N^+CH_3 + −CON−CH_2− + −CH_2−N^+ + −CH_2−N−aryl), 6.5−7.5 (CH aryl), 7.7 (−CONH−).

The NMR spectrum shows no visible signal indicating residual dimethylamino groups. Integration of the signals at 2.8−4.1 ppm and at 6.5−7.5 gives an estimate content of $x \approx 0.4$ of the repeat units with the aniline group in the copolymer. In good agreement, the content x in copolymer **12** was determined to be $x = 0.34$ by UV/vis spectroscopy, using an extincion coefficient of $\epsilon = 9.41 \times 10^3$ L mol^1 cm^{-1} as measured for *N*-acryloyl-*N′*-phenylpiperazine.

*Synthesis of copolymer **14**.* *N*-Ethyl-*N*-[2-(11-bromoundecanoyl)oxyethyl]aniline is made from 4-bromoundecanoic acid and 2-(*N*-ethylanilino)ethanol by condensation with dicyclohexyl carbodiimide as described above for *N*,*N*-bis(2-(4-bromobutanoyl)oxyethyl)aniline. Purification by flash chromatography (eluent: petrol ether/ethyl acetate 15v/1v). Yield 86% of slightly yellowish oil, $n_D^{22} = 1.522$. ^1H NMR (200 MHz, $CDCl_3$, δ in ppm): 0.7−1.9m (−$(CH_2)_8$− + N−C−CH_3), 2.20t (2H, −CH_2−COO−), 3.05−3.7 m (6H, Br−CH_2− + −CH_2−N−CH_2−), 4.1t (2H, −COO−CH_2−), 6.4−6.8m (3H, CH aryl o- and p-position), 7.10m (2H, CH aryl, m-position). 0.696 g (1.69 mmol) of *N*-ethyl-*N*-[2-(4-bromoundecanoyl)oxyethyl]aniline and 1.00 g (5.88 mmol of repeat unit) of polymer **7** are stirred in 10 mL of dry DMF under argon at 60 °C for 3 days. Then, the mixture is reacted with 1.3 mL of bromoethane at 40 °C for 48 h. The polymer is precipitated in ethyl acetate, dried in vacuo, dissolved in water, and lyophilized. Yield of polymer **14**: 1.75 g of colorless, very hygroscopic powder.

Microanalysis: 47.03% C, 7.96% H, 8.63% N, 24.98% Br.

^1H NMR (200 MHz, d_6-DMSO, δ in ppm): 0.5−1.6 (−CH_3 backbone + −$(CH_2)_8$− + aryl−N−C−CH_3), 1.9−2.7 (−CH_2− backbone + −CON−C−CH_2− + −CH_2−COO− + solvent), 2.9−3.9 (N^+CH_3 + −CON−CH_2− + −CH_2−N^+ + −CH_2−N−CH_2− + water), 4.2 (−COO−CH_2−), 6.8−6.95 (CH aryl), 7.25 (CH aryl), 8.1−9.0 (−CONH−).

The complex NMR spectrum does not allow to quantify the copolymer composition by integration of the signals. Qualitatively, there is no visible signal indicating the presence of unmodified dimethylamino groups, pointing to their absence. In agreement, the missing IR band at 2780 cm^{-1} of the tertiary dimethylamine moieties of precursor **7** suggests the nearly complete conversion of the tertiary amine groups. From the Br content by microanalysis, the content of repeat units bearing aniline groups x is calculated to be $x = 0.14$. In reasonable agreement, the content x in copolymer **14** was determined to be $x = 0.19$ by UV/vis spectroscopy, using an extincion coefficient of $\epsilon = 2.01 \times 10^4$ L mol^1 cm^{-1} as measured for *N*-ethyl-*N*-phenylethanolamine.

*Synthesis of Polymer **16**.* Monomer *N*-(2-methacryloyloxyethyl)-4-methylpyridinium bromide (**15**) was prepared from bromoethanol, methacryloyl chloride, and 4-methylpyridine, analogously to the synthesis of **17**.[24] Hygroscopic, slightly yellowish oil, $n_D^{22} = 1.542$.

^1H NMR (200 MHz, $CDCl_3$, δ in ppm): 1.85s (3H, =C−CH_3), 2.7s (3H, aryl−CH_3), 4.7t (2H, −COO−CH_2−), 5.4t (2H, −CH_2−N^+), 5.6d (1H CH=C−COO trans), 6.1d (1H CH=C−COO cis), 7.85d and 9.35d (2H + 2H, CH aryl).

1.0 g (3.5 mmol) of monomer **15** is polymerized in 15 mL of water at 70 °C for 72 h, using 4.7 mg of $K_2S_2O_8$ as initiator. Precipitation into acetone, dissolution in water, and lyophilization gives 0.74 g of solid, colorless, hygroscopic polymer **16**.

Microanalysis ($[C_{12}H_{16}BrNO_2]_n$, $M_r = [286.17]_n$): Calcd for monohydrate: 47.39% C, 5.96% H, 4.60% N, 26.27% Br. Found: 47.42% C, 5.95% H, 4.20% N, 25.82% Br.

^1H NMR (200 MHz, D_2O, δ in ppm): 0.4−0.9 (−CH_3 backbone), 1.1−1.9 (−CH_2− backbone), 2.6 (aryl−CH_3), 3.9−4.4 (−CH_2−N^+), 4.4−5.2 (−COO−CH_2− + HDO), 7.9 and 8.55 (CH aryl).

*Synthesis of Polymer **18**.* 0.98 g (2.3 mmol) of monomer **17** is polymerized in 15 mL of water at 70 °C for 24 h, using 9.4 mg of initiator VA552. Precipitation into acetone, redissolution in water, and lyophilization gives 0.87 g of solid, slightly yellowish, hygroscopic polymer **18**.

^1H NMR (200 MHz, D_2O, δ in ppm): 0−2.1 (−CH_3 backbone + −$(CH_2)_9$− + −CH_2− backbone), 2.45 (aryl−CH_3), 3.8−4.2 (−COO−CH_2−), 4.2−5.0 (−CH_2−N^+ + solvent), 7.8 and 8.65 (CH aryl). The signals of the protons in the alkyl chain and of the ones close to the backbone are strongly broadened, whereas the signals assigned to the pyridinium ring are rather narrow.

*Synthesis of Polymer **20**.* 2.87 g (18.8 mmol) of 4-chloromethylstyrene, 4.69 g (50.4 mmol) of 4-methylpyridine, and 2 drops of nitrobenzene in 80 mL of dry ethanol are refluxed for 48 h. The solvent is evaporated, and the residue is purified by flash chromatography (eluent: $CHCl_3$/methanol 5v/2v) to give 2.0 g (43%) of yellowish, hygroscopic oil of *N*-(4′-vinylbenzyl)-4-methylpyridinium chloride, **19**, $n_D^{22} = 1.5731$.

^1H NMR (200 MHz, D_2O, δ in ppm): 2.6s (3H, aryl−CH_3), 5.3d (1H, CH=C−aryl cis), 5.6s (2H, N^+−CH_2−aryl), 5.8d (1H, CH=C−aryl trans), 6.7m (1H, =CH−aryl), 7.3d (2H, CH aryl), 7.5d (2H, CH aryl), 7.8d (2H, CH aryl), 8.6d (2H, CH aryl).

0.80 g (3.3 mmol) of monomer of *N*-(4′-vinylbenzyl)-4-methylpyridinium chloride (**19**) is polymerized in 20 mL of water at 60 °C for 3 days, using 15 mg (0.033 mmol) of initiator VA552. Precipitation into acetone, redissolution in water, and lyophilization gives 0.70 g of solid, colorless, very hygroscopic polymer **20**.

^1H NMR (200 MHz, D_2O, δ in ppm): 0.8−2.1 (−CH− and −CH_2− backbone), 2.3 (aryl-CH_3), 5.6 (N^+−CH_2−aryl), 6.5 (CH aryl), 7.3 (CH aryl), 7.7 (CH aryl), 8.7 (CH aryl).

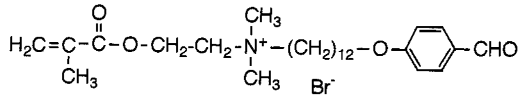
Coupling Agents. The sodium salts of phenylhydrazine-4-sulfonic acid (**21**), 4-nitroaniline-3-sulfonic acid (**22**), 7-aminonaphthalene-1,3-disulfonic acid (**24**), the chloride of 4-diazo-1,1′-azobenzene-3,4′disulfonic acid (**25**), and 5-formylfuranesulfonic acid (**26**) were commercial products (Aldrich) and were used as received. The sodium salt of 4-(2′-amino-5′-nitrophenyloxy)butanesulfonic acid (**23**) is prepared as follows: 3.00 g (19.5 mmol) of 2-amino-5-nitrophenol in 30 mL of dry THF is slowly neutralized by NaH. 2.65 g (19.5 mmol) of 1,4-butanesultone in 20 mL of dry THF is slowly added at ambient temperature, and the mixture is refluxed overnight. The solvent is removed to give the crude product. Purification by flash chromatography (silica gel, eluent: $CHCl_3$/methanol 5v/2v) yields **23** in form of a yellowish, highly viscous oil. ^1H NMR (200 MHz, D_2O, δ in ppm): 1.8m (4H, −CH_2−CH_2−), 2.9t (−CH_2−SO_3), 4.0t (−O−CH_2−), 6.7d (CH aryl, position 3), 7.5s (CH aryl, position 6), 7.7 (CH aryl, position 4).

Anilines are converted into the diazonium salts as exemplified for 4-nitroaniline-3-sulfonic acid (**22**): 9.11 g (33 mmol) of **22** is dissolved in the heat in 10 mL of 5 N HCl. The mixture is cooled to 0 °C. To the resulting suspension is added dropwise a cooled solution of 2.28 g (33 mmol) of $NaNO_2$ in 10 mL of water. After 10 min of additional stirring at 0 °C, urea is added to destroy the residual HNO_2, allowing for 15 min of stirring. The mixture is ready for use and can be stored at below 5 °C for 48 h without losing its activity.

Activation of Adsorbed Layers. Addition of bisulfite onto aldehydes: the coatings are exposed to a saturated solution of $NaHSO_3$ in water at ambient temperature for 10 min. Condensation of phenylhydrazines with aldehydes: the coatings are exposed to a saturated solution of phenylhydrazine-4-sulfonic acid (**20**) in 30% aqueous acetic acid at room temperature. Azocoupling: the coatings are exposed to the solution of the diazonium salt at about 5 °C for 30 min. Condensation of *N*-alkyl-4-methypyridinium salts with aldehydes: after adsorbing a layer of the reactive polycation, the supports are heated for 30 min in a 6×10^{-3} M solution of 5-formylfuranesulfonic acid (**25**) and of equimolar amounts of triethylamine, either in methanol at reflux or in ethylene glycol at 80 °C. Coupling of Reactive Black 5 (**32**) onto polymeric amines: supports are immersed alternatingly into a solution of polyvinylamine for 20 min at ambient temperature, into aqueous NaOH (pH = 9) for 4 min, and into 0.5×10^{-3} M solution of **31** in 10^{-2} M K_2CO_3 (pH = 10) for 40 min at 80 °C.

Methods. NMR spectra were recorded by models Gemini-200 and a Gemini-300 (Varian). IR spectra were taken from KBr pellets (model 205, Nicolet). UV/vis spectra were taken by a SLM AMINCO DW-2000 spectrometer. Viscometric measurements were performed by an Ubbelohde capillary

Table 1. Polycations Functionalized with the *p*-Alkoxybenzaldehyde Moiety and Their Intermediates



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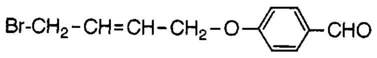

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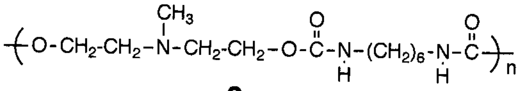
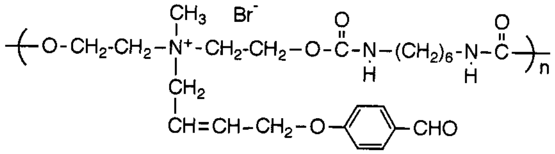


$$-\!\left[O-CH_2-CH_2-N(CH_3)-CH_2-CH_2-O-C(=O)-NH-(CH_2)_6-NH-C(=O)\right]_n-$$

3



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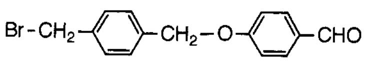

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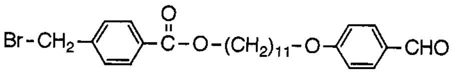

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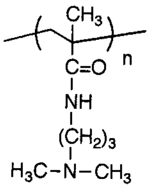
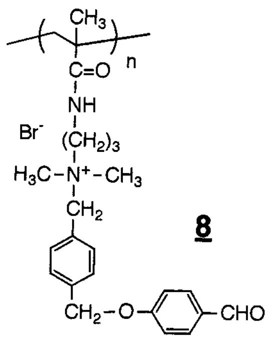


$$-\!\left[CH_2-C(CH_3)(C(=O)-NH-(CH_2)_3-N(CH_3)_2)\right]_n-$$

7



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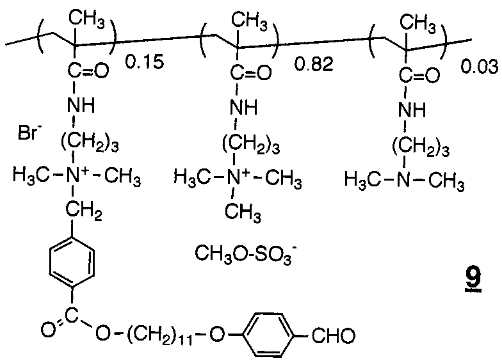


9

viscometer AV 500 (Schott). Time-of-flight secondary ion mass spectroscopy (ToF−SIMS) were taken as described elsewhere.[28]

Quartz (Suprasil) and glass slides were used as supports. They were cleaned with a 1v:1v mixture of concentrated sulfuric acid and 30% H_2O_2 at 80 °C for 20 min. Then they were rinsed with water and placed into a mixture of concentrated aqueous ammonia, 30% H_2O_2 and water (1v:1v:5v) at 80 °C for 30 min. Subsequently, they were precoated with one monolayer of poly(ethyleneimine) and one monolayer of poly(vinyl sulfate) or poly(sulfopropyl methacrylate) as "primer" layer, as described before.[16] Polyelectrolytes were typically adsorbed for 20 min from 10^{-2} M (based on the repeat unit) aqueous solutions. In the case of polymer **9**, 4×10^{-2} M (referred to as the repeat unit) aqueous solutions were employed. After each adsorption step or activation step, the supports are immersed three times into freshwater for 1 min.

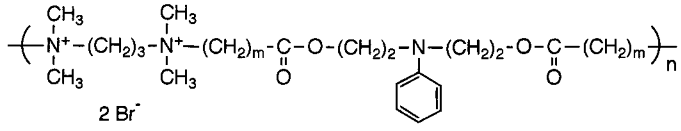
Results and Discussion

Polymer Synthesis. The reactive polymers employed and their intermediates are presented in Tables 1 and 2. The most direct access to cationic polyelectrolytes is the free radical polymerization of charged monomers, such as **1, 15, 17,** and **19**. However, whereas the incorporation of the 4-methylpyridinium moiety into the polymers **16, 18,** and **20** by free radical polymerization is straightforward, the incorporation of the aniline group is not evident, and the one of the benzaldehyde group is even less obvious. Aldehydes are efficient radical inhibitors, as are (trace) oxidation products of aniline. Hence, the failure of the attempts to polymerize the aldehyde containing monomer **1** were not surprising. As a consequence, polymers **4**, **8,** and **9** were prepared by modification of precursor polymers containing tertiary amine groups. For this purpose, benzaldehydes **2**, **5,** and **6** were synthesized which are functionalized by allyl and benzyl bromide groups. These moieties were chosen to render the alkylations of the polymers close to quantitative while avoiding harsh conditions (Figure 3). This strategy allowed the incorporation of spacer groups of variable length, separating the ammonium and the aldehydes moieties, too. As polymers **4** and **8** were insoluble in pure water (though soluble in DMSO/water mixtures), precursor polymer **7** was only partially functionalized by reagent **6** containing a long hydrophobic spacer, in order to avoid insufficient hydrophilicity of the final polymer. The residual dimethylamino groups were quaternized by dimethyl sulfate in a second step, to provide a water-soluble polymer. Nevertheless, the strong broadening of the ^1H NMR signals of the protons of the undecyl fragment as well as of aromatic protons in D_2O compared to the spectra taken in DMSO suggests hydrophobic association of the functional side groups, as in micellar polymers.[29]

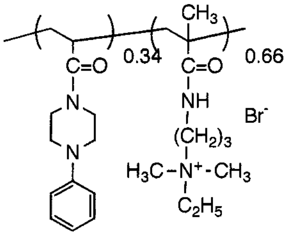
Polycations **13** and **14** bearing the tertiary aniline moiety were prepared following the same strategy as discussed above for polymer **9**. Alternatively, aniline bearing polymers **10** and **11** were prepared by polycondensation, in analogy to standard ionenes.[30] The two polymer pairs of **10** and **11** and of **13** and **14** were designed to enable investigations on the influence of the localization of the cationic groups, in the backbone or in the side chain, on the CoMPAs process. Simultaneously, they should allow to study the influence of the length of spacer groups.

In the polymer series **16**, **20,** and **18**, the 4-methylpyridinium moiety is increasingly separated from the backbone by a spacer group. As found for polymer **9**, the signals of the protons of the alkyl chain and of the backbone of polymer **18** are strongly broadened in D_2O. This is once more attributed to hydrophobic association of the side groups, keeping in mind that **18** can be identified by its molecular structure as a classical

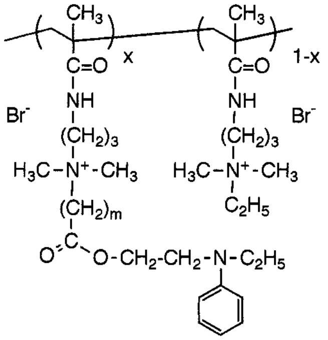
Table 2. Polycations Functionalized with the Aniline Moiety or with the 4-Methylpyridinium Moiety and Their Intermediates



10: m = 3 **11**: m = 10

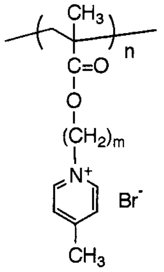


12



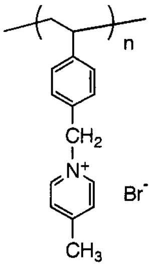
13: x = 0.33, m = 3

14: x = 0.19, m = 10



16: m = 2

18: m = 11



20

polysoap,[29] in analogy to poly(*N*-(11-methacryloyloxyundecyl)pyridinium bromide) and closely related polycations.[31−33]

Due to their polyelectrolyte character, and mostly additionally aggravated by the presence of association inducing groups (by hydrophobic interactions or by H-bonding), a direct determination of the molar masses of the polymers studied could not be performed. Whereas for the polymers prepared (directly or indirectly) by free radical polymerization molar masses should be reasonably high, this is not evident for polymers **4, 10,** and **11** made by polycondensation. In particular in the case of ionenes, low oligomers cannot be excluded a priori. Viscometric studies of the three polymers yielded typical polyelectrolyte behavior, i.e., a minimum at intermediate concentrations with increasing reduced viscosities at low concentrations. Polyurethane **4** yielded a minimum value of $\eta_{red} = 300$ mL/g at a concentration of about 20 g/L in DMSO, suggesting reasonably high molar masses and/or association. The uncharged precursor polymer **3** has an intrinsic viscosity of $[\eta] = 71$ mL/g in DMSO. Ionene **10** yielded a minimum value of $\eta_{red} = 20$ mL/g at a concentration of about 30 g/L in water. Ionene **11** yielded a minimum value of $\eta_{red} = 45$ mL/g at a concentration of about 30 g/L in methanol. Also, no signals of $-CH_2Br$ end groups and only traces of signals at 2.9 ppm—putatively attributed to protonated $-CH_2-N(CH_3)_2$ end groups—were detected by ^{1}H NMR (Figure 4). Therefore, we concluded that the polymers are not low molar mass oligomers, though very high molar masses are not probable, given the properties of ionenes in general.[30]

Thermogravimetric analysis of the polycations indicated thermal stability up to about 190 °C (under nitrogen, heating rate 10 °C/min), above which degradation starts. No glass transition could be found by differential scanning calorimetry for the polymers below of the thermal decomposition.

Multilayer Construction Using Aldehyde Bearing Polymers. The restauration of the negative charge in the adsorption/activation cycle is based on the addition of the HSO_3^- anion onto aldehydes to yield the α-hydroxysulfonic acid (cf. Figure 2). The reaction requires typically concentrated solutions of $NaHSO_3$ which is poorly soluble in organic solvents. Therefore, pure water or mixtures of water/DMSO 3v/1v were used for the experiments. As polymer **8** is not well soluble under such conditions, studies were focused on polymers **4** and **9**. Note that **4** bears an equal number of cationic ammonium and reactive aldehyde groups, whereas in **9** the cationic groups outnumber the aldehyde moieties by far.

The addition of HSO_3^- destroys the conjugated donor−acceptor π-system of the 4-alkoxybenzaldehydes. Thus, the bathochromic band in the absorbance spectra disappears. In the case of the solution of polymer **4** in water/DMSO 3v/1v, the band with $\lambda_{max} = 280$ nm is gradually diminished by addition of $NaHSO_3$, while a new band with $\lambda_{max} < 238$ nm of the resulting phenol ether emerges gradually. Analogously, the UV band of **9** with $\lambda_{max} = 280$ nm (solution in water) decreases upon addition of the $NaHSO_3$. Also, a new UV band at shorter wavelengths appears that superposes the UV band of the benzoate moiety with $\lambda_{max} = 230$ nm. The direct quantification of the conversion of the reactive chromophore by measuring the change in absorbance at 280 nm must assume that the addition of bisulfite to the benzaldehyde groups is independent of their relative orientation to the substrate and thus to the probing UV beam. Though this assumption seems probable, it has to be used with care.

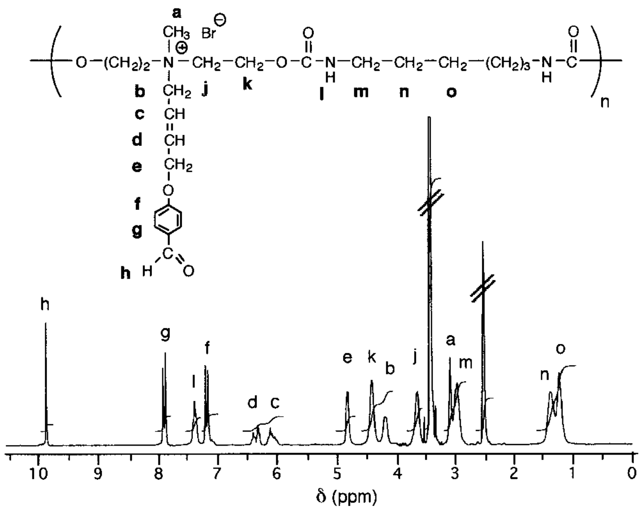


Figure 3. ^{1}H NMR spectrum of polymer **4** in DMSO-d_6. Signals of the solvent are marked //.

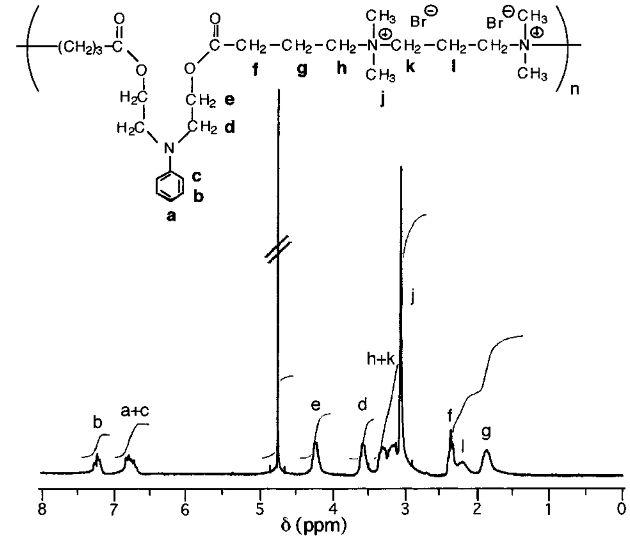


Figure 4. ^{1}H NMR spectrum of polymer **10** in DMSO-d_6. Signals of the solvent are marked //.

Figure 5 illustrates the evolution of the UV spectra of coatings obtained from **4** by the CoMPAS method. The spectra indicate successful and continuous layer buildup, as seen by the growth of the band at about 230 nm. This finding is qualitatively corrobated by ToF−SIMS studies of the adsorbed films, after the adsorption and after the activation step. The ratio of the signal at the mass of $m = 80$, indicative of the SO_3 fragment, compared to the one of $m = 77$, indicative of the phenyl fragment, increases strongly after the activation step. In contrast, no spectral changes are observed when supports that had been submitted to an adsorption but not yet to an activation cycle are immersed into the polycation solutions for a second time. This demonstrates that the activation step is crucial for the film growth.

The addition of the bisulfite anion is very fast. The reaction is finished in less than 3 min, as UV spectra taken after 3 and 20 min are identical. Therefore, for all subsequent experiments, the addition reaction was limited to 10 min.

Figure 5 shows the increase of the UV band at about 230 nm with increasing adsorption/activation cycles, whereas the band at 280 nm evolves sluggishly only, if at all, when monitored after the activation step. Although the evolution of the 230 nm band indicates the regular overall growth of the multilayers, the presence and slow growth of the 280 nm band points to a major, though incomplete, consumption of the aldehyde moiety by the activation cycle. Also, the activation reaction seems to be not fully regular. This might be due to the reversibility of the bisulfite addition, keeping in mind that all adsorption and activation steps are followed by multiple rinsing of the supports with clean water.

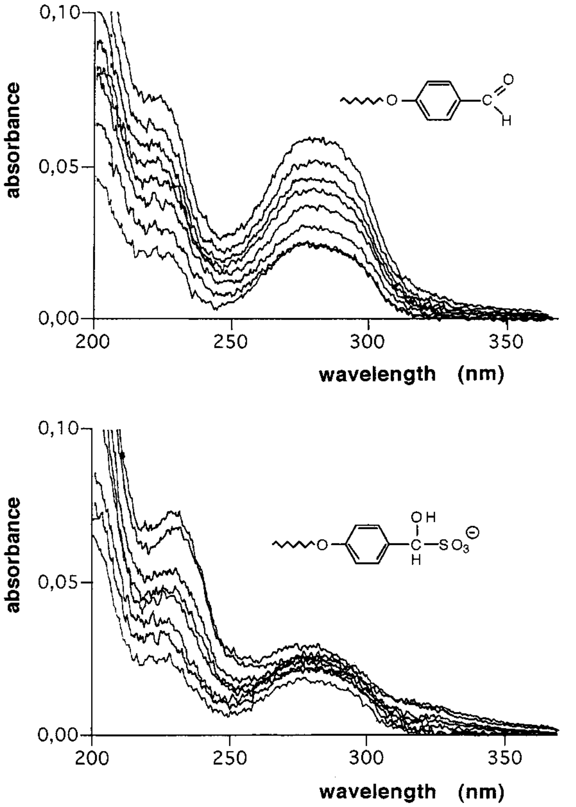


Figure 5. UV spectra of multilayers made from polymer **4** by CoMPAS: (a, top) spectra taken after the adsorption step; (b, bottom) spectra taken after the activation step using $NaHSO_3$.

The approximately linear increase of the 280 nm band when monitored after the adsorption step is surprising at first sight. We attribute this behavior to the reversibility of the bisulfite addition during the rather long adsorption step of the polyelectrolyte, even in lower layers. This leads to an equilibrium between aldehyde and α-hydroxysulfonic acid in the film. The liberated aldehyde groups and possibly some of the residual aldehyde groups are (re)consumed in subsequent activation cycles. The possibility of such a “postactivation” of reactive groups in underneath layers was demonstrated by using multilayers made by alternating deposition of polyelectrolytes of opposite charge, e.g., employing polycation **4** and polyvinyl sulfate. The thicker the layers are, the more important is the loss of the absorbance at 280 nm upon exposure to aqueous $NaHSO_3$. This demonstrates the rapid penetration of the bisulfite anion even into lower layers.

Polymer **9** used for multilayers by CoMPAS provides similar results as polymer **4** (Figure 6). The UV band centered at 231 nm derives to a large extent from the benzoate spacer group. This band allows to follow the regular growth of the multilayer films, in addition to the conversion of the benzaldehyde which is indicated by the consumption of the 280 nm band.

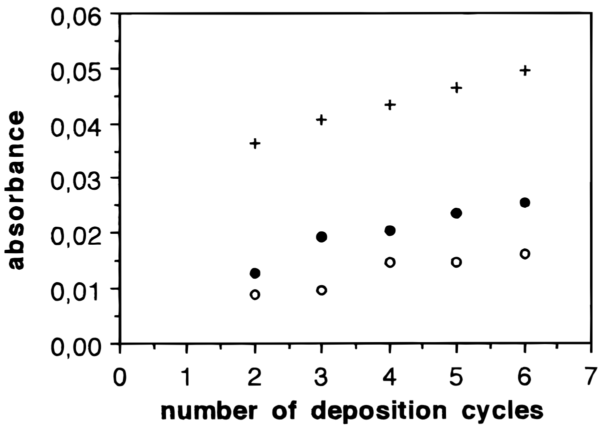


Figure 6. Absorbance of CoMPAS multilayers from polymer **9** using $NaHSO_3$, at 231 nm (+), at 281 nm after the adsorption step (●), and at 281 nm after the activation step (○).

The successful use of polymer **9** is remarkable for several reasons. First, the polymer seems to undergo hydrophobic, presumably intramolecular association in water, like for polysoaps.[29] This association in the solution obviously does not interfere with regular deposition onto the support, implying a conformational change upon adsorption. Second, the content of aldehyde groups is only about 15% compared to the one of cationic groups fixed to the polymer. Even complete conversion, which is obviously not the case, could not yield an electrically neutral polyzwitterion (as in the case of **4**) but still would provide an overwhelmingly positively charged polyampholyte. Despite this apparently unbalanced situation, multilayer growth by CoMPAS works. Therefore, we must presume a net orientation of the hydrophobized polycation in a mixed adsorbed polyelectrolyte/hydrophobic monolayer conformation. Such an arrangement would present the polar benzaldehyde fragments preferentially at the aqueous interface, whereas the hydrophobic spacers are somewhat hidden in the layer. Thus, the incorporation of only some sulfonate groups will suffice to reverse the surface charge and to enable continuous multilayer buildup.

Though the ease and the high speed of the bisulfite addition to aldehydes seems very satisfactory for the CoMPAS process, the reversibility of the reaction and the difficulties in rationalizing the UV spectra led us to explore alternative systems. Different from the addition of the bisulfite anion which results in the loss of the bathochromic band of the absorbance spectra of the system, thus indicating conversion only, coupling reactions that create a new chromophore while adding negatively charged groups onto the cationic polymer were studied. In such systems, the evolution of the absorbance resulting from the activation reaction can be easily followed and quantified. This allows to verify the reproducibility of the successive activation and adsorption steps.

In this context, the coupling of the aldehyde moiety with 4-hydrazinebenzenesulfonic acid (**21**) in half-concentrated acetic acid was attempted, aiming at the reversal of the surface charge via the formation of the sulfonated hydrazone chromophore (cf. Figure 2). In homogeneous solution, the reaction with hydrazine (**21**) yields the yellow solution of the corresponding sulfonated hydrazone, replacing for example the absorbance maximum of **9** of $\lambda_{max} = 280$ nm by the hydrazone band with a maximum at $\lambda_{max} = 355$ nm. However, the hydrazone coupling could not be applied successfully for multilayer growth by CoMPAS with the aldehyde functionalized polymers studied. Attempts to react **21** with adsorbed polycations bearing an aldehyde moiety neither did produce colored coatings, as expected, nor did allow further regular adsorption of polycations.

Speculating about the reasons for the failure of the hydrazone coupling for CoMPAS, the use of an organic solvent for the coupling however seems not to be a major handicap, as evidenced by the successful application of the CoMPAs method in aqueous DMSO (see above) or in various alcohols (see below). However, we note that the reaction is already slow in solution. This might be caused by the low solubility of the zwitterionic reagent **21** in the reaction medium, which possibly renders the surface reaction inefficient.

Multilayer Construction Using Aniline Bearing Polymers. The tertiary aniline residues of polymers **10**−**14** can be easily converted into azo dyes by coupling under mild conditions. Using diazonium salts derived from sulfonated arylamines such as **22**−**25** (Table 3), the coupling adds negatively charged groups to the cationic polymers, while creating a strong dye. As discussed above, the evolution of color by the activation reaction allows to record the stepwise buildup of multilayers and to verify their regular growth. However, different from the use of the benzaldehydes for CoMPAS, the superposition of the UV band of the arylamine by the absorbance of the newly formed dye at short wavelengths interferes with a quantification of the conversion.

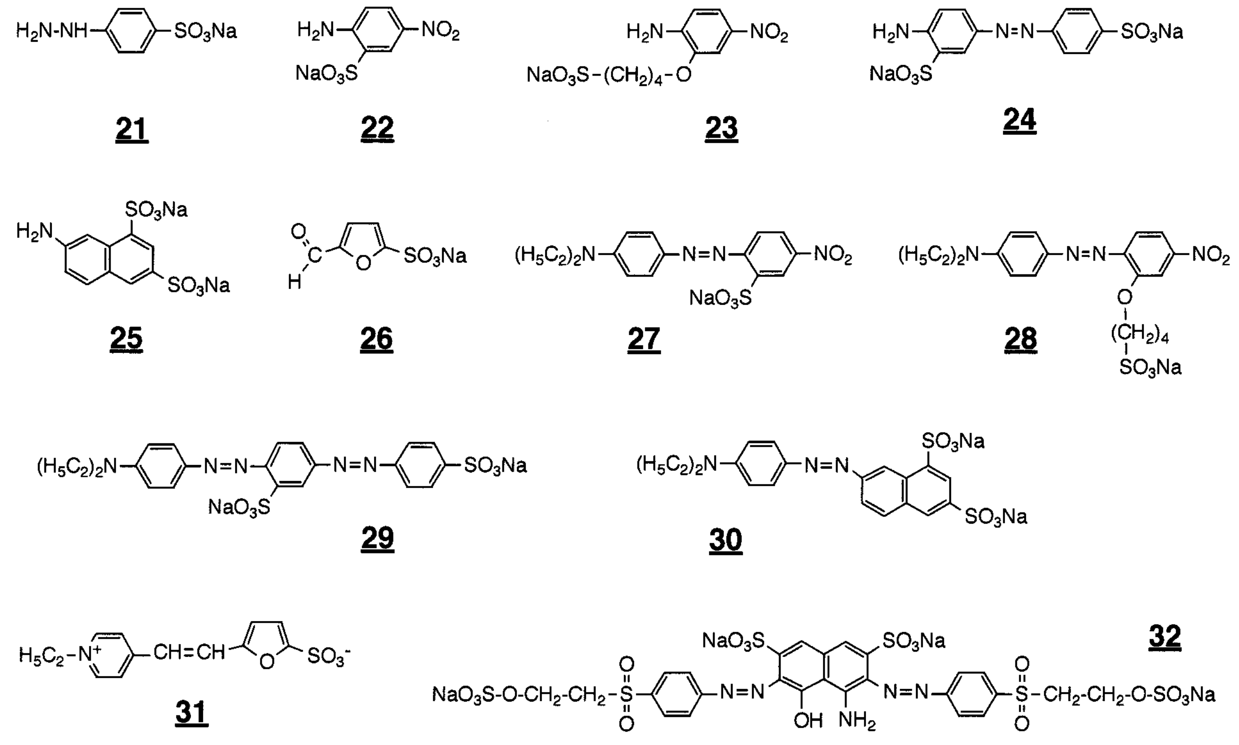
Figures 7−10 exemplify the evolution of the UV spectra of coatings obtained from various polycations activated by the a series of diazonium salt, indicating a continuous layer growth. Continuous layer growth by adsorption/activation cycles of polymers **10**, **11,** and **13** with the diazonium salt of **22** was evidenced by ToF−SIMS and by X-ray reflection, too.[22,23,34] As discussed above for the use of aldehyde functionalized polycations in CoMPAS, the activation step is crucial for continuous growth. If the supports are submitted to an adsorption step only, but the successive activation step is omitted, a repeated immersion of the support does not lead to spectral changes, which would indicate further layer growth.

The azo coupling of the anilines is less rapid than the addition of HSO_3^- on aldehydes. Maximum coloration is typically obtained after 60 min of exposure to the supports to diazonium salt solutions of **22**−**25**. However, such a prolonged reaction produces turbid layers, for unknown reasons. Therefore, the activation step by azo coupling was limited to 30 min for all subsequent experiments. This provides already good coloration (about 80% of the maximal intensity), enables successive adsorption of the polycations, and yields clear coatings in general.

By adhering to this procedure, it cannot be excluded that the activation of the aniline groups in the newly adsorbed polycation layer is accompanied by a "postactivation" of residual aniline groups in underneath layers. Such a reaction would increase the overall coloration of the films, but it should not interfere with multilayer growth.

As discussed above for the polymers bearing aldehyde groups, such a "postactivation" of not yet consumed reactive groups in underneath layers is rather probable. Polyelectrolyte multilayers prepared by alternating

Table 3. Low Molar Mass Reagents Used for the Activation of Adsorbed Layers, and the Reference Dyes Resulting from Their Reaction with Diethylaniline, or *N*-Ethyl-4-methylpyridinium Bromide, Respectively



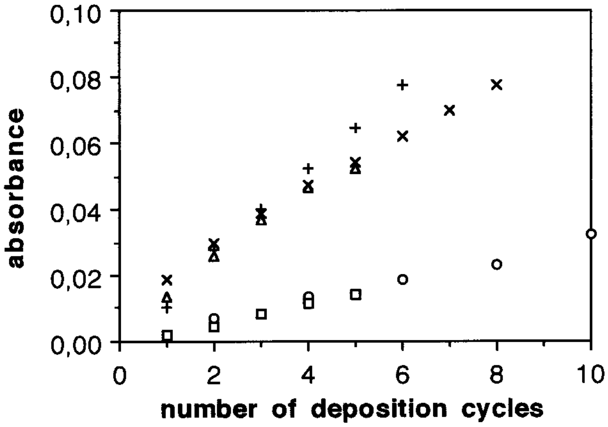


Figure 7. Absorbance of CoMPAS multilayers from polycations bearing tertiary anilines using the diazonium salt of aniline **22**: polymer **10** (○, λ = 440 nm); polymer **11** (□, λ = 445 nm); polymer **12** (△, λ = 470 nm); polymer **13** (+, λ = 480 nm); polymer **14**, λ = 480 nm (×).

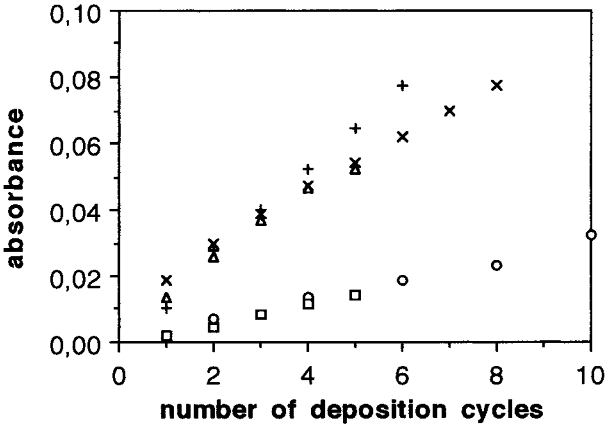


Figure 8. Absorbance of CoMPAS multilayers from polycation **13** using the diazonium salts of various anilines: **23** (+, λ = 500 nm); **24** (○, λ = 450 nm); **25** (×, λ = 450 nm).

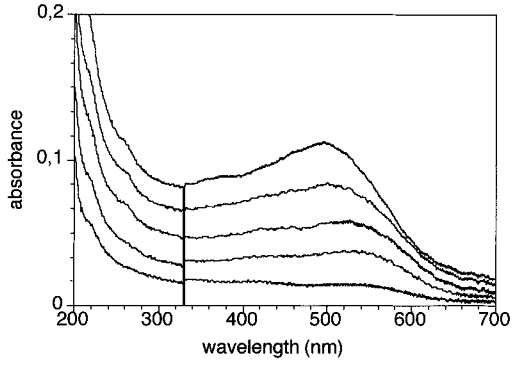


Figure 9. UV/vis spectra of CoMPAs multilayers from polymer **13** and the diazonium salt of aniline **23** (1–7 layers).

deposition of polycation **13** and of poly(sulfopropyl methacrylate) allowed to evidence the penetration of the diazonium salts into lower layers. When exposing such polyelectrolyte multilayers for 30 min to the diazonium salt of nitroaniline, the absorbance at 497 nm of the formed azo dye increases with increasing multilayer thickness, though the increase per layer pair becomes smaller for thicker layers (Figure 11). This demonstrates the rapid diffusion even of bulkier ions into the water-swollen multilayers, as found previously for small ions[35] and for fluorescence quenchers.[36] Also, the increasing difficulty of the reagents to react with anilines in deeper layers parallels the finding of analogously decreasing efficiencies of mobile quenchers for buried fluorophores[36] which were attributed to a compacting of interior layers.

Multilayers could be grown by the CoMPAS method for all combinations studied. However, some difficulties showed up for the diazonium salt of **23** and for polymer **12**. The use of **23** led to homogeneously colored multilayers, but thicker films became turbid. Multilayer

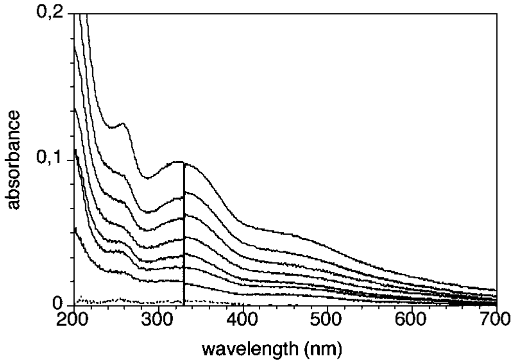


Figure 10. UV/vis spectra of CoMPAs multilayers from polymer **13** and the diazonium salt of aniline **24** (1−5 layers).

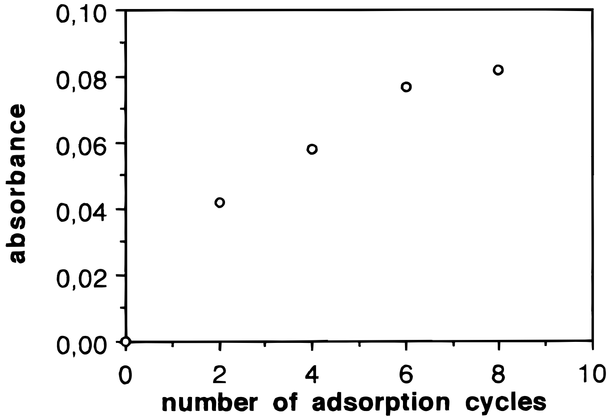


Figure 11. Influence of the overall multilayer thickness on the efficiency of the activation reaction: maximum absorbance at λ = 497 nm after reacting the diazonium salt of 4-nitroaniline with polyelectrolyte multilayers made by alternating deposition from poly(sulfopropyl methacrylate) and polycation **13**.

growth with **12** was not linear: the increase in absorbance becomes smaller with increasing number of adsorption/activation cycles (cf. Figure 7). For the other systems, CoMPAS led to continuously growing, homogeneously colored, clear multilayers.

A closer look at the UV/vis spectra of the multilayers grown by CoMPAS reveals some pecularities. The azo coupling of the studied polymers in solution yielded for low conversions colored solutions with absorbance maxima λ_{max} close to the ones found for the parent dye, i.e., the azodye made from diethylaniline and the employed diazonium salt (Table 4). At high conversions, however, a moderate hypsochromic shift of the absorbance maximum shows up in a number of cases (Table 4, Figure 9). In grown multilayers, the values of λ_{max} are dramatically shifted to even much shorter wavelengths. In fact, when comparing the coupling products of polymers **10**−**14** with the diazonium salt of **22**, λ_{max} varies from polymer to polymer used (Table 4). The most important hypsochromic shifts are found for ionenes **10** and **11**, i.e., for the polymers incorporating the aniline moiety in the backbone. Additionally in the case of **11**, λ_{max} fluctuates notably from layer to layer within 435 and 460 nm, if multilayer growth is followed spectroscopically step by step. The next important spectroscopic shift is observed for polymer **12**, i.e., the one with the shortest spacer group between aniline moiety and backbone. Polymers **13** and **14** behave rather similarly, exhibiting the least pronounced shifts. Polymer **13,** however, activated by the diazonium salt of aniline **23** exhibits a marked hypsochromic shift with increasing film growth (Figure 9). In contrast, if the bulky diazonium salts **24** and **25** are used, the multilayers show only diffuse absorbance bands in the visible spectrum without clear maxima (Figure 10).

Table 4. Absorbance Maxima of the Activated Polymers in Aqueous Solution and in CoMPAS Multilayers

dye	aniline	coupling agent	$\lambda_{max}(H_2O)$ (nm)	λ_{max}(coating) (nm)
27	*N*,*N*-diethylaniline	**22**	523	
28	*N*,*N*-diethylaniline	**23**	520	
29	*N*,*N*-diethylaniline	**24**	513	
30	*N*,*N*-diethylaniline	**25**	490	
	10	**22**	523	450
	11	**22**	523	445[a]
	12	**22**		470
	13	**22**	512−504[b]	498
	14	**22**	510−503[b]	490
	13	**23**	517	540−490[c]
	13	**24**	495	bb[d]
	13	**25**	450−410[b]	bb[d]
	10	**25**	454	bb[d]

[a] Fluctuation of λ_{max} by ±15 nm. [b] Continuous hypsochromic shift of λ_{max} with increasing conversion. [c] Continuous hypsochromic shift of λ_{max} with increasing cycles. [d] Broad band without clear maximum.

The observed hypsochromic shifts are too strong to be explained by simple solvatochromism. Instead, aggregation of the dyes is most probable, as found for some polyelectrolyte multilayers[19,21]—though in a much less dramatic manner. As this complication shows up for all the diazonium salts studied, the aggregation cannot be primarily due to the donor−acceptor substitution pattern of some of the dyes formed. Rather, the combination of complementary charges on the chromophores and on the residual polymer seems to be a major driving force. In agreement with this explanation, the importance of the effects is correlated to the proximity of the dyes to the polymer backbone, as discussed above. But whatever the reasons, the aggregation of the chromophores may create a number problems in practice. For example, the irregular increase in nonlinear optical activity of CoMPAS layers made from polymers **10, 11,** or **13** with the diazonium salt of **22** reported in the past[22,23] can at least in part be attributed to the aggregation of the chromophores.

The reasons for the success of the activation/adsorption cycles are not fully clear yet. Even complete activation of the aniline residues results in the case of **10** and **11** in a ratio of 2 cations vs 1 anion in the adsorbed polymers. For polymers **12**−**14**, the situation is even less balanced. In fact, polymer **11** coupled with diazotated aniline **22** in solution before adsorption behaves as on overall polycation, as expected: multilayer growth from this modified polymer is not possible; however, it may be employed as polycation in the alternating adsorption of polyelectrolytes.[16] Hence as discussed for the aldehyde functionalized polymer **9** above, we must deduce a preferential orientation of the functionalized polycations in a such a way that the reactive moieties are concentrated at the surface. Again, a mixed adsorbed polyelectrolyte/hydrophobic monolayer conformation is probable, presenting the polar reactive groups preferentially at the water interface. Due to this accumulation, the incorporation of some sulfonate groups can suffice to guarantee continuous multilayer buildup. This picture is qualitatively supported by studies of the ζ-potential of multilayers made by the CoMPAS method, which oscillates from positive to negative values after the adsorption and after the activation step, respectively.[22]

Interestingly, this picture seems to differ from the model of well-interdigitated polyelectrolyte layers as proposed for the structure for multilayers prepared from polyelectrolytes of opposite charge.[15] Such an arrangement would imply neutralization of the newly introduced negative charges on the polymer by the cationic counterparts which are present in large excess; this is obviously not the case.

The uneven distribution of reactive groups within the adsorbed layers implies a basic noncentrosymmetric film structure. Therefore, the CoMPAS process can allow to prepare functional noncentrosymmetric films, which are notoriously difficult to achieve. Although not compulsory, a noncentrosymmetric orientation of the chromophores formed in the deposition process should be thus possible, similar to the forced noncentrosymmetric orientation of chromophores in self-assembled multilayers.[12,13] In fact, by virtue of the high second-order nonlinear polarizability of the dyes made with the diazonium salt of **22**, i.e., derivatives of the dye disperse red, second harmonic generation could indeed verify the orientation of the newly formed chromophores in certain cases.[22,23]

Multilayer Construction Using 4-Methylpyridinium Bearing Polymers. Similar to the azocoupling on anilines, the condensation of 4-methylpyridinium salts with aromatic aldehydes creates strong chromophores (cf. Figure 2) which facilitate to follow the growth of the multilayers. Polycations such as **16, 18,** and **20** bearing the 4-methylpyridinium moiety have the advantage that the cationic and reactive groups become identical. This simplifies the structure of the resulting polymers considerably.

The reactions of polymers **16, 18,** and **20** worked smoothly in methanol, ethanol, or ethylene glycol with various aldehydes, but the condensation always yielded insoluble products. This type of aldol condensation is best catalyzed by secondary amines,[37] whereas tertiary amines are much less efficient. Still, the use of secondary amines was not satisfactory for the condensation in the adsorbed layers. Possibly, the large excess of secondary amine in the liquid phase blocks the aldehyde completely in the form of the enamine. In contrast, the much slower catalysis by tertiary amines worked in solution as well as in the adsorbed layers, if high amine concentrations are used.

Out of polymers **16, 18,** and **20**, only the latter two enabled to build up multilayers by condensation with 5-formyl-2-furanesulfonic acid (**26**). All attempts to react **26** with adsorbed polycation **16** gave at maximum a very faintly colored coating which did not allow further polycation adsorption. Given the similarity of polymers **16** and **18**, we attribute the failure to the very short, i.e., not sufficiently long, spacer group between the polymer backbone and the 4-methylpyridinium moiety. In contrast, homogeneously colored multilayers could be easily grown from **18** (Figure 12) as well as from **20** by CoMPAS.[23] These findings illustrate the high potential of the CoMPAs method, as for the coupling rather harsh conditions were used, such as organic solvents and elevated temperatures, without causing the coatings to detach.

Different from the multilayers obtained by the CoMPAS method via azo coupling, the multilayers made via aldol condensation did not show marked spectroscopic shifts of the dyes prepared in situ. The low molar mass parent dye **31** made from *N*-ethyl-4-methylpyridinium bromide and 5-formyl-2-furanesulfonic acid (**26**) shows an absorbance maximum in water of $\lambda_{max} = 376$ nm, whereas the multilayers prepared from polymers **18** and **20** exhibit absorbance maxima at 388 and 383 nm, respectively. As additionally the absorbance bands appear to be symmetrical, there is no indication of important chromophore aggregation.

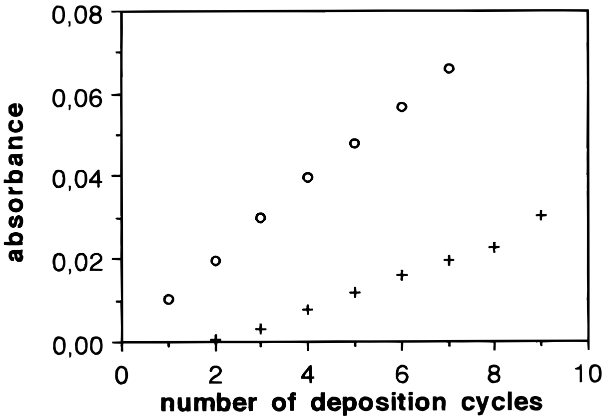


Figure 12. Absorbance of CoMPAS multilayers made from polycation **18** using aldehyde **26** (○, $\lambda = 388$ nm) and from polyvinylamine with reactive dye **32** (+, $\lambda = 603$ nm).

Nevertheless, the use of organic solvents is not unproblematic for CoMPAS multilayers. The colored multilayers obtained are homogeneous to the eye and in the optical microscope, but thicker layers made of polymer **20** become increasingly turbid. The same is true for multilayers of **18** grown in methanol, whereas layers prepared in ethylene glycol stay clear. The observed turbidity might be a consequence of the poor solvating power of organic solvents, even of alcohols, for polyzwitterions,[38,39] leading to the collapse of the swollen adsorbed polycations.

There seems to be another problem of the CoMPAS method performed at elevated temperatures in organic solvents. Similar to the azo dyes discussed above, the donor−acceptor chromophore **31** prepared should be well suited for nonlinear optical purposes, such as second-harmonic generation (cf. refs 40−42). But films made of polymer **18** activated with **26** did not show second-harmonic generation, different from films made of polymeric anilines activated with **22**. Possibly, the elevated temperatures of the activation reaction induce a randomization of the orientation of the chromophores.

Multilayer Construction Using Reactive Dyes. The dying of fibers by attaching covalently reactive dyes is well established. Many of such dyes bear negatively charged groups, to improve water solubility.[43] Obviously, such dyes may be suited for the CoMPAS method exploiting for example the attack of polymer bound nucleophiles on halogenated triazines or on the activated double bonds of vinyl sulfones, as formed in situ by treating for example dye **32** with base. Particularly promising nucleophiles attached to polymers are primary and secondary amines, which upon (partial) protonation may simultaneously serve as cationic groups. This simplifies the structure of the reactive polymers enormously, even compared to the 4-methylpyridinium based systems, thus allowing for the use of "standard" polymers. Somewhat different from the azocoupling of anilines or from the condensation of 4-methylpyridinium salts with aldehydes, the success of the CoMPAS coupling reaction is not directly evident: the multiple charged dye could only adsorb physically onto the polycations without covalent coupling which in special cases can allow classical multilayer buildup.[16,44−46]

Preliminary studies with polymeric amines such as poly(ethyleneimine), polyallylamine, polyvinylamine, or chitosane demonstrated the feasibility of the reactive dye approach for CoMPAS, as exemplified for dye **32** and polyvinylamine in Figure 12. Absorbance growths linearly, with the absorbance maximum slowly shifting bathochromically from 600 to 606 nm with increasing thickness of the films ($\lambda_{\mathrm{max}} = 597$ nm in water). As leaching of the colored multilayers by water or by brine did not lead to a decrease of absorbance (cf. refs 16, 45, and 46) or to coloring of the leaching solutions, we conclude that the fixation of dye **32** is indeed covalently and is not due to electrostatic interactions. Albeit small, the spectroscopic shift observed suggests once more some aggregation of the dyes.

Conclusions

The new CoMPAS method is well-suited for the construction of defined multilayers, employing a variety of parent polymers and reactive groups. Most interestingly, the multilayers obtained will inherently exhibit a noncentrosymmetric structure, although this does not necessarily imply the orientation of functional fragments. The reactive polymers needed must essentially contain ionic fragments and polar reactive groups. Additional spacer groups separating the polymer backbone and the reative fragments seem to be advantageous. Presumably, the spacers help the reactive groups to accumulate at the film surface, as needed in order to obtain charge reversal at the surface. The multilayers formed adhere well on the supports and on themselves. The method works under mild conditions, such as low temperature and in aqueous solution. But it tolerates organic solvents and elevated temperatures, too. So, the method is rather flexible and may be suited for many purposes. From the examples of successful systems presented here, we assume that a number of other coupling reactions will be found useful for CoMPAS in the future.

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