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Aggregation Phenomena in Polyelectrolyte Multilayers Made from Polyelectrolytes Bearing Bulky Functional, Hydrophobic Fragments

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Summary: The functionalization of polyelectrolyte multilayers often implies the use of bulky functional fragments, attached to a standard polyelectrolyte matrix. Despite of the high density of non-charged, often hydrophobic substituents, regular film growth by sequential adsorption proceeds easily when an appropriate polyelectrolyte counter ion is chosen. However, the functional fragments may cluster or aggregate. This complication is particularly evident when using chromophores and fluorophores as bulky pendant groups. Attention has to be paid to this phenomenon for the design of functional polyelectrolyte films, as aggregation may modify crucially the properties. The use of charged spacer groups does not necessarily suppress the aggregation of functional side groups. Still, clustering and aggregation depend on the detailed system employed, and are not obligatory. In the case of cationic poly(acrylamide)s labeled with naphthalene and pyrene fluorophores, for instance, the polymers form intramolecular hydrophobic associates in solution, as indicated by strong excimer formation. But the polymers can undergo a conformational rearrangement upon adsorption so that they are decoiled in the adsorbed films. Analogous observations are made for polyanions bearing mesogenic biphenyls fragments. In contrast, polycations functionalized with the dye coumarin 343 show little aggregation in solution, but a marked aggregation in the ESA films.

Keywords: electrostatical self-assembly; functional polyelectrolytes; hydrophobic aggregation; layer-by-layer; polyelectrolyte multilayers

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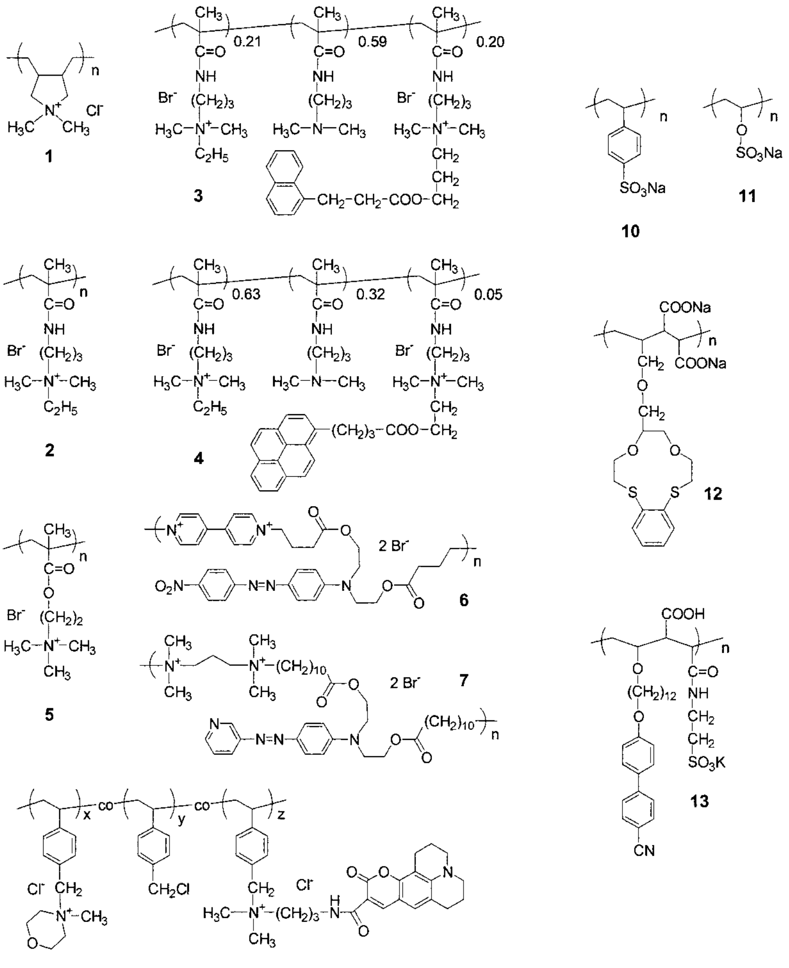
Introduction

The layer-by-layer assembly of oppositely charged polyelectrolytes into ultrathin films, often named electrostatical self-assembly (ESA), has been well established in the past decade.[1-4] Developed only in the early 1990ies, many fundamental studies have been published since, and numerous potential applications have been proposed. A closer look to these developments shows that the vast majority of the work has been focused on a few standard polyelectrolytes only. Functionality for various uses has been mainly based on the sheer presence of the films (volume and barrier effects), on their surface modification, or on their patterning. Relatively little work has been dedicated yet to functional ESA films in which the function derives from molecular functionality of the constituting polyelectrolytes, i.e. to ESA films made of polyelectrolytes bearing functional groups. This is for sure partially due to the challenges inherent in the synthesis of complex polyelectrolytes. But moreover, the wide-spread opinion that a critical charge density is needed to prepare ESA films[5-8] seems to have discouraged the design of chemically functionalized systems: complex functional groups are in general rather bulky, rather hydrophobic, and bear only few, or more often even no charged moieties. Fortunately, this opinion is not justified as exemplified in several studies. Rather than a critical charge density, the matching of the charge density of the polyelectrolyte pair is needed for successful ESA film growth.[9-11] Thus, appropriate selection of the polyelectrolyte *pairs* used allows the preparation of most different functional systems.[10-20] Still, the arrangement of the functional fragments in the films may pose problems, depending on the context. On the one hand, the functional fragments may be isotropically or anisotropically distributed within the films, and their alignment and orientation is difficult to control. On the other hand, the low polarity of the functional fragments, - compared to the ionic groups -, favours their aggregation and clustering. This is not only a matter of homogeneity or inhomogeneity on a given scale, but aggregation and clustering may drastically modify, or may even interfere with the desired functionality of chemical fragments.[18-24] This problematic is frequently overlooked.

We have therefore studied the use of several functionalized polyelectrolytes for ESA, bearing chromophores and fluorophores. Such functional groups may probe their own environment, thus providing information about possible aggregation phenomena. The standard and functional polyelectrolytes used are shown in Table 1.

Table 1. polycations (**1-9**) and polyanions (**10-13**) used



8 x=0.70 y=0.27 z=0.03 **9** x=0.86 y=0.08 z=0.06

Experimental part

Materials

For all experiments, deionized water was purified by an Elgastat Maxima or a Millipore purification system (resistance 18.2 MΩ). Flash chromatography was performed on silica gel (Merck, 230-400 mesh). Branched poly(ethyleneimine) and poly(sodium 4-styrene-sulfonate) were purchased from Aldrich and used without further purification. Poly[diallyldimethylammonium chloride] **1** was a gift from W. Jaeger (FhG-IAP, Golm). Poly[sulfonyl ethyl maleic acid monamide-*alt*-4'-cyanobiphen-4-yl-oxydodecyl vinyl ether] **13** was a gift of A. C. Nieuwkerk and A. T. M. Marcelis (Wageningen Agricultural University).[25] The synthesis of polymers **2**, **5**-**7**, and of poly[(sulfopropyl)methacrylate] was described previously.[26-28] The synthesis of polymers **8**, **9** and **12** will be described elsewhere.[29,30]

Synthesis of polycation **3**: Following a standard procedure,[31] 1.00 g (5.81 mmol) of 2-(naphth-1-yl)ethanol, 0.97 g (5.81 mmol) of 4-bromobutyric acid and 0.100 g of 4-dimethylaminopyridine in 30 ml of dry CH_2Cl_2 are cooled to 0 °C. A solution of 1.20 g (5.82 mmol) of dicyclohexylcarbodiimide in 5 ml of dry CH_2Cl_2 is added drop wise. After cooling for another 5 h, the reaction mixture is stirred for 24 h at ambient temperature. The precipitated dicyclohexylurea is filtered off, and the solvent is evaporated. The crude 2-(naphth-1-yl)ethyl-4-bromobutanoate obtained is purified by flash-chromatography (eluent: $CHCl_3$) to yield 1.4 g (75%) of colourless powder. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.1 (m); 7.7.5-7.95 (m); 7.3-7.6 (m) [1H+2H+4H, CH aryl]; 4.46 (t) [2H, -CH_2O-]; 3.35-3.50 (m) [2H+2H,-CH_2Br, -CH_2-aryl]; 2.49 (t) [2H, -CH_2-COO-]; 2.13 (m) [2H, -C-CH_2-C-]. 0.19 g (0.59 mmol) of 2-(naphth-1-ylethyl)-4-bromobutanoate and 1.00 g (5.87 mmol) of poly[(3-N,N-dimethylaminopropyl)methacrylamide] are dissolved in a mixture of 10 ml of ethanol and 10 ml of nitromethane and stirred at 60 °C for 36 h under argon. Then, 0.79 ml of bromoethane (ρ=1.460, 10.6 mmol) are added and the mixture is stirred for 48 h at 40 °C. The resulting polymer **3** is precipitated into ethyl acetate, dissolved in ethanol and precipitated once more into ethyl acetate. Yield: 0.84 g (71%) of colourless hygroscopic powder.

Synthesis of polycation **4**: 0.25 ml (0.434 g; 3.47 mmol) of 2-bromoethanol, 1.00 g (3.47 mmol) of 4-pyren-1-ylbutyric acid and 0.04 g of 4-dimethylaminopyridine in a mixture of 20 ml of dry CH_2Cl_2 and 7 ml of dry THF are cooled to 0 °C. A solution of 0.716 g (3.47 mmol) of dicyclohexylcarbodiimide in 5 ml of dry CH_2Cl_2 is added drop wise. The cooling is maintained for 5 h and then the reaction mixture is stirred at ambient temperature for 24 h. After filtration of the precipitated dicyclohexylurea, the solvent is evaporated. The crude (2-bromoethyl)-4-pyren-1-yl-butanoate is purified by flash-chromatography (eluent: toluene), to yield 1.8 g (94%) of white solid. ^{1}H-NMR (200MHz, $CDCl_3$): δ = 7.7-8.35 (m) [9H, aryl]; 4.40 (t) [2H, -CH_2O-]; 3.35-3.55 (m) [4H,-CH_2Br, -CH_2-aryl]; 2.51 (t) [2H, -CH_2-COO-]; 2.21 (m) [2H, -C-CH_2-C-]. Polycation **4** is prepared from 1.00 g (5.87 mmol) of poly[(3-N,N-dimethylaminopropyl)-methacrylamide] and 0.23 g (0.59 mmol) of (2-bromoethyl)-4-pyren-1-ylbutanoate in analogy to polymer **3**. Yield: 0.92 g (75%) of colourless, hygroscopic solid.

Methods

NMR spectra were taken with a Gemini-200 spectrometer (Varian). UV/VIS spectra of the multilayer assemblies on quartz were recorded with a SLM-AMINCO DW-2000 spectrophotometer in the double beam mode, or with a spectrophotometer CARY 5E (Varian). A clean quartz plate served as reference. Ellipsometry was performed using polished Si-wafers as support with a Multiskop (Optrel GmbH, Berlin, Germany), assuming a refractive index of 1.5. Stationary fluorescence excitation and emission spectra were recorded with a 48000S SLM AMINCO spectrofluorometer and with a Fluorolog-3 spectrofluorometer Jobin Yvon – Spex system from Instruments S.A., Inc. (USA). A front-face configuration was used to record the spectra of the multilayer films. The spectra were corrected for the wavelength dependence of the detector. The X-ray reflectivity measurements were performed with a Siemens D5000 diffractometer for incidence angles lower than 4.5°, using a Cu-K_α radiation and a secondary graphite monochromator. A good collimation of the beam was achieved by placing a knife-edge a few µm above the sample surface. The data were corrected for background scattering and variation of the illuminated area at very low angles of incidences. Data were analyzed by fitting a model consisting of a succession of thin sublayers on flat substrate using a matricial iteration formalism derived from Fresnel equations.[6]

Preparation of the polyelectrolyte multilayers

An automatic dipper (Kirstein & Riegler, Berlin, Germany) was used for the alternating polyelectrolyte deposition, working at room temperature in glass beakers without stirring.

Multilayer films were built on fused quartz plates, or on polished Si-wafers. The polyions were dissolved in water with a concentration of 10^{-2} mol repeat unit per liter. Only in specified cases, HCl was added at a concentration of 10^{-2} M. The quartz plates used as substrates for the multilayers were cleaned as described.[32] Occasionally, initial buffer layers of cationic branched poly(ethyleneimine), anionic poly[(sulfopropyl)methacrylate] and cationic **7** were deposited onto the quartz substrates prior to the deposition of the systems studied. Multilayers were assembled by alternating dipping of the substrates into the solutions of the polycations and polyanions for 20 min each. Before changing the polyelectrolyte solutions, the substrates were rinsed by dipping into pure water three times for 1 min, to remove adhering excess solution. The resulting films made of x layer pairs, e.g. of polymers **2** and **10**, will be named $\{\mathbf{2/10}\}_x$ in the following.

Results and Discussion

Polyelectrolyte multilayers can be easily grown from standard polyelectrolyte pairs with high charge density, for instance polymer films $\{\mathbf{1/10}\}_x$, $\{\mathbf{1/11}\}_x$, or $\{\mathbf{2/10}\}_x$. Also, more complex polyelectrolytes, such as polyanion **12** bearing a crown ether can be easily deposited with polycation **1**, despite the high content of the uncharged crown fragment in the polymer (Figure 1). Following film growth by ellipsometry, regular, linear growth is observed (Figure 1a). However, thicker films tend to become turbid and the increase in optical density is no more linear (Figure 1b). Apart from other putative explanations, one may ask whether non-coulombic forces between the bulky and hydrophobic functional fragments may be responsible. In the UV-spectra, no change in the general spectral properties is observed so that there is no indication of special interactions. Still, one would not expect the simple chromophore to be sensitive to changes of its environment. But of course, a possible clustering of the crown ether unit might have important consequences for its complexation properties, for instance whether 1:1 or sandwiched 2:1 complexes would be formed with metal cations. Unfortunately, it is very difficult to derive in such systems information on the local arrangement of the functional groups, namely of the crown ethers in the films.

In order to obtain local structural information, - at least qualitatively -, we have looked into hydrophobically substituted polyelectrolytes, where the functional groups themselves can be used as probes, namely they are solvatochromic chromophores or fluorophores.

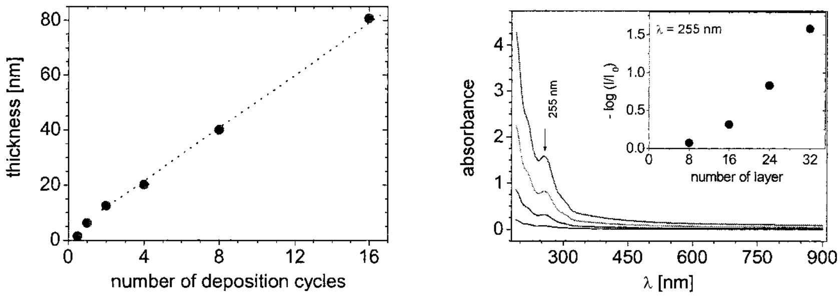


Figure 1. Growth of multilayers {**1/12**}$_x$, as followed by (a) ellipsometry and by (b) UV-Vis spectroscopy: from bottom to top: 8, 16, 24 and 32 deposition cycles; inset: absorbance at λ= 255 nm as function of the number of deposition cycles x

A particularly interesting question arises when the modified polyelectrolytes that are employed for ESA films, are known to undergo hydrophobic aggregation in dilute aqueous solution. The general usefulness of some micellar polymers for the layer-by-layer deposition technique has been demonstrated before.[10, 26, 33-36] But it is not clear how the associative character in solution influences the structure of the adsorbed film, e.g. whether hydrophobic domains are preserved upon adsorption, as found in the case of bipolar amphiphiles,[37-40] or whether not.

The hydrophobically substituted polycations, **3** and **4** (see Table 1), can nicely illustrate the problem. Alike their unlabeled parent polymer **2**, both were prepared by quaternization from the same batch of precursor poly[(3-N,N-dimethylaminopropyl)methacrylamide], in order to have an identical degree of polymerization, thus avoiding eventual effects due to different molar masses. The ^{1}H NMR spectra of polymers **3** and **4** (Figure 2) show that the quaternization of the amino groups is not complete. Whereas the signal at 3.0 ppm is assigned to the protons of the methyl groups of the quaternized ammonium group, the signal at 2.85 ppm is assigned to the protons of the residual tertiary dimethylamine groups, which are mostly protonated in water. From the integration of the ^{1}H-NMR signals, the compositions of the tercopolymers were estimated. The ratio of the integrals of the signal of the aromatic protons and of the signals of the protons in the range of 3.6-2.5 ppm was used in the case of copolymer **3**. Similarly for copolymer **4**, the ratio of the integrals of signal of the aromatic protons and of the signals of the protons in the range of 3.5-2.6 ppm was used. The contents of hydrophobic substituents for copolymers **3** and **4** were accordingly estimated to be 20 mol-% naphthalene groups and 5 mol-% of pyrene groups, respectively.

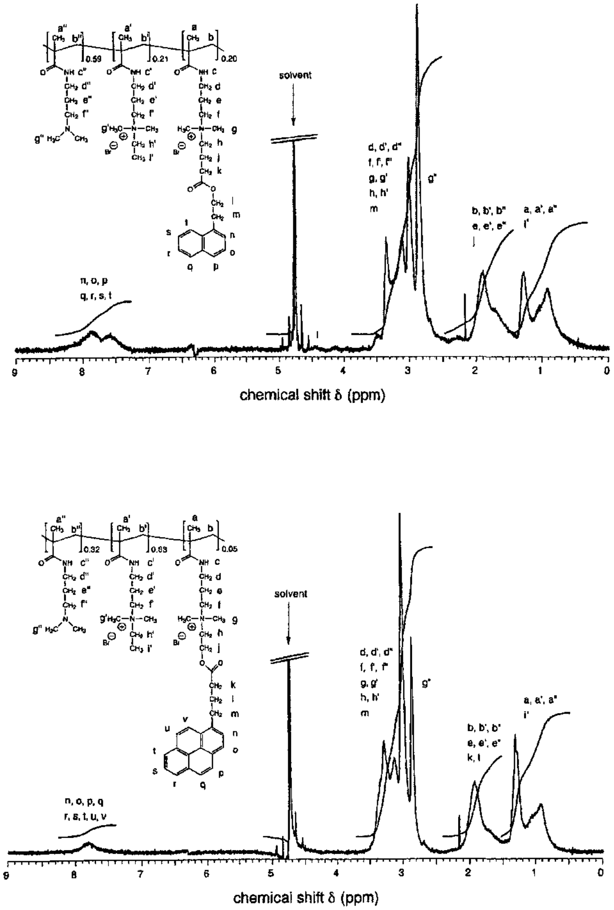


Figure 2. ^{1}H-NMR spectra of polycation **3** (a) and **4** (b) in D_2O

The choice of naphthalene and pyrene residues as hydrophobic groups offers the advantage that both are good fluorophores, so that they can simultaneously serve as probes. However, the residual tertiary amine groups due to the incomplete quaternization of the precursor polymer can quench the emission of the fluorophores. Though under ambient conditions (pH ≈ 5.8), the tertiary amines are expected to be mostly protonated in water, beforehand studies revealed still a notable increase in fluorescence intensity when reducing the pH value to 1 (Figure 3). This is attributed to the complete conversion of the residual amine groups into the hydrochloride form at low pH. Further addition of HCl increases the fluorescence intensities of the copolymers only slightly. Note that the shape of the emission spectra (see below) was not changed by the pH. The increase in fluorescence intensity is more pronounced for polymer **3** than for **4**, in agreement with the higher sensitivity of naphthalene to quenching by amines compared to pyrene.[41, 42]

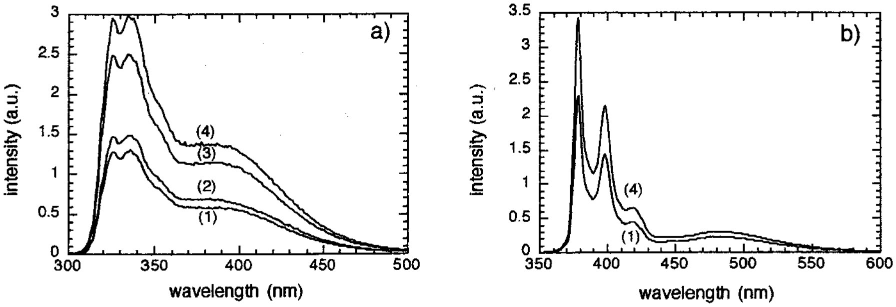


Figure 3. Fluorescence emission spectra of polymers **3** (a) and **4** (b) in 10^{-2} M solution in (1): water; (2): 10^{-3} M HCl ; (3): 10^{-2} M HCl ; (4): 10^{-1} M HCl . Excitation at 290 nm for **3** or at 340 nm for **4**, respectively

Interestingly, the emission spectrum of copolymer **3** in aqueous solution shows not only the usual fluorescence band of the naphthyl group from 310 nm to about 400 nm with two maxima at 335 nm and 345 nm, but also an additional marked shoulder centered at about 390 nm (Figure 3a). The excitation spectra of the solution recorded at 335 nm, 420 nm and 440 nm correspond all to the absorption spectrum of polymer **3** in water. Therefore, the formation of a naphthalene dimer in ground state must be excluded. We assume the formation of a naphthalene excimer although such excimers are rare. But as the content of naphthyl groups in **3** is high, the formation of hydrophobic domains favouring excimer formation is most plausible.[43, 44] Analogously, the fluorescence emission spectrum of copolymer **4** in aqueous solution is characterized by the structured main emission between 350 nm and 450 nm, and an additional broad unstructured band centered at about 470 nm (Figure 3b). This band is assigned to the excimer of the pyrene,[45] suggesting hydrophobic association in water.

Polyanion **10** and the precursor polycation **2** are known to form layer-by-layer films of high quality.[26] Layer-by-layer assemblies of polyanion **10** with the functionalized analogs polycation **3**, or with **4** respectively, were first prepared from pure aqueous solutions, providing visually transparent films. The absorption band of **10** at 226 nm was used to monitor the regularity of the deposition process, because the absorbance of the naphthyl and pyrenyl groups were - though easily visible in the spectra - too low to quantify precisely the deposition process. Both systems $\{\mathbf{10/3}\}_x$ and $\{\mathbf{10/4}\}_x$ exhibit a linear increase of the absorbance with the number of deposition cycles (Figure 4), indicating a regular deposition process.

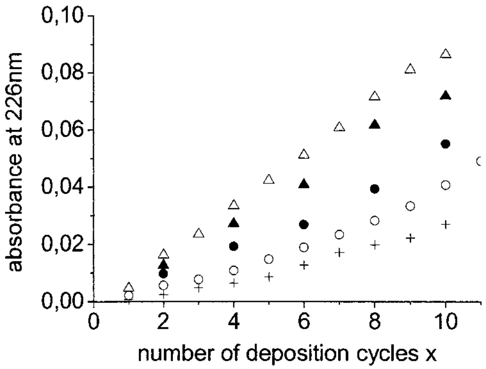


Figure 4. Growth of layer-by-layer assemblies $\{\mathbf{10/3}\}_x$ (△, ▲) and $\{\mathbf{10/4}\}_x$ (○, ●), followed by the absorbance of **10** at 226 nm. Open symbols: films grown from aqueous solutions. Closed symbols: films grown from 10^{-2} M HCl solutions. Data for the films $\{\mathbf{10/2}\}_x$ made from aqueous solutions are added for comparison (+)

The amount of deposited polyanion **10** increases in the multilayer system $\{\mathbf{10/3}\}_x > \{\mathbf{10/4}\}_x > \{\mathbf{10/2}\}_x$. Still, the density of charged groups in polycations **3** and **4** is close to the one in polycation **2**, and the degree of polymerization is the same. The thicker films in the case of the system $\{\mathbf{10/3}\}_x$ may result from a notable contribution of hydrophobic interactions[26] or of favorable π-π interactions to layer growth, as the high number of naphthalene residues in **3** should well match with the phenyl groups of polyanion **10**. But though multilayer films can be grown regularly from pure aqueous solutions, the intensities of the fluorescence emission of these two systems $\{\mathbf{10/3}\}_x$ and $\{\mathbf{10/4}\}_x$ were very low with estimated quantum yields below of 1%, especially for the naphthalene based system. We attribute this finding to the high content of amino groups in the polymers which results in an efficient fluorescence quenching. Therefore, layer-by-layer assemblies were prepared from solutions of the cationic polymers in 10^{-2} M HCl, while the polyanion **10** was adsorbed from pure aqueous solutions as otherwise non-linear growth took place. In order to avoid any problem of intermediate storage of the films for higher deposition cycles (*cf.* ref. 26), a series of samples was prepared without any drying step. Again, the absorbance at 226 nm grows linearly with the number of dipping cycles, indicating the regularity of the process (Figure 4). As observed for films prepared from pure water, more **10** is adsorbed in $\{\mathbf{10/3}\}_x$ films than in $\{\mathbf{10/4}\}_x$ ones. However, the amount of polyanion **10** adsorbed varies when changing the pH. In the case of the system $\{\mathbf{10/3}\}_x$, slightly less polymer is adsorbed when depositing from 10^{-2} M HCl, in the case of the system $\{\mathbf{10/4}\}_x$, slightly more polymer is adsorbed. This somewhat surprising finding is attributed to two opposite effects which are superposed: the increase in ionic strength typically leads to thicker layers, whereas an increasing content of ionic groups, due to the increasing protonation of the residual amines with decreasing pH, results in thinner layers.[2] Apparently, the balance of these two effects is different for polycations **3** and **4**. In the case of polycation **3** with a high content of amines, the effect of increasing protonation seems to dominate, whereas in the case of polycation **4** with a low content of amines, the effect of increasing ionic strength seems to prevail.

The multilayers grown from 10^{-2} M HCl solutions show indeed improved fluorescence intensities, so that the environment of the hydrophobic groups may be probed. Most noteworthy, the emission spectra of the $\{\mathbf{10/3}\}_x$ films show the absence of excimer emission in the naphthalene fluorescence (Figure 5). Similarly, no pyrene excimer emission is found for films $\{\mathbf{10/4}\}_x$

(Figure 6 and Figure 7). These systems are thus suited e.g. for Förster Resonance Energy Transfer experiments, taking advantage of the spectral match of the naphthyl and pyrenyl groups.[46] In fact, sequentially deposited films like **[10/4/10/3]**$_x$ and **[10/4/10/2/10/3/10/2]**$_x$ exhibit a strong pyrene emission at about 417 nm, compared to a low naphthalene emission in the region of 320 nm - 370 nm when excited at 290 nm. This is the wavelength where the absorbance by naphthalene chromophore compared to pyrene absorbance is maximized. For comparison, no pyrene fluorescence could be detected for the reference system **[10/4]**$_{10}$ when excited at 290 nm. Still, one has to keep in mind that quantum yields are low, so that it cannot rigorously be excluded that the fluorophores might not probe the average situation.

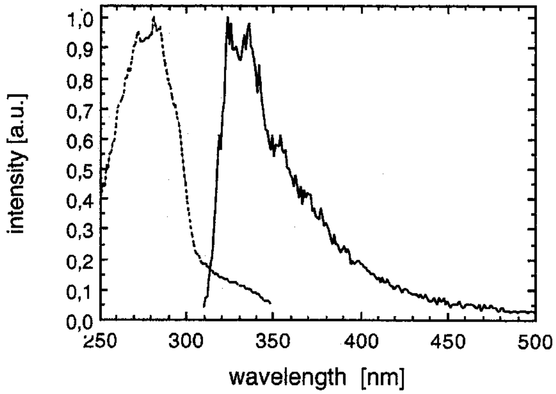


Figure 5. Excitation (---) and emission (____) spectra of layer-by-layer assemblies {**10/3**}$_{10}$. Excitation and emission wavelengths are 290 nm and 372 nm, respectively

The fluorescence of these systems exhibits the peculiarity that shape of the emission spectra varies with time. Freshly prepared samples {**10/4**}$_x$ show a ratio of the intensity of the vibronic peaks I_1/I_5 of the emission band of about 1 (Figure 6). Samples stored for a few days exhibit a ratio of I_1/I_5 of about 1.5 (Figure 7). A closer look to the spectra shows that the ratio I_1/I_5 of freshly prepared films increases already slightly with the number of deposited layers (Figure 6). Although for substituted pyrenes, the ratio of I_1/I_5 is normally no more an accurate measure of the local polarity, it still provides a rough indication for it, thus suggesting a considerably more polar environment of the chromophores after annealing at room temperature.[47]

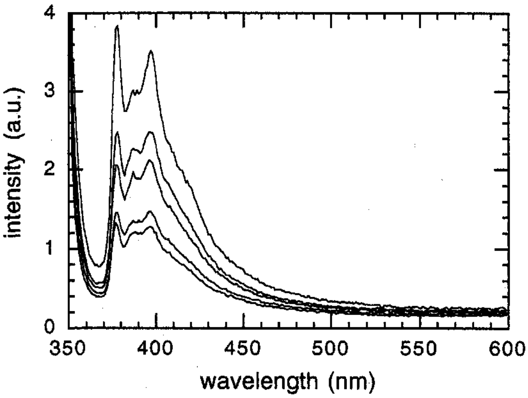


Figure 6. Emission spectra of freshly prepared layer-by-layer assemblies {**10/4**}$_x$. From bottom to top: x = 2, 4, 6, 8, 10 (Excitation at λ_{exc}= 345 nm)

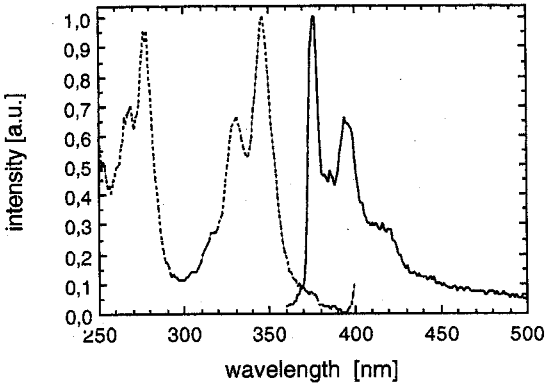


Figure 7. Excitation (---) and emission (____) spectra of stored films {**10/4**}$_{10}$. Emission and excitation wavelengths are 417 nm and 347 nm, respectively

Two important conclusions impose from these spectral features, concerning the aggregation of the bulky hydrophobic fragments. First, the absence of excimer fluorescence suggests the disruption of the hydrophobic domains upon adsorption for both polymers **3** and **4**. This means that the polymers do not adsorb in the form of more or less deformed coils, let alone of micellar structures. In contrast, they seem to decoil efficiently when adsorbing on the support and to take an extended conformation. This interpretation is corroborated by X-ray reflectivity measurements performed on the polyelectrolyte films, providing thicknesses of less than 0.5 nm per polyanion-polycation layer pair, i.e. showing very thin adsorption layers. Second, the evolution of the ratio I_1/I_5 with storage indicates a continuous rearrangement of the polyelectrolyte complexes. Note that such a rearrangement is not reflected in the UV-absorbance spectra. There have been some other occasional reports about such rearrangements in the past, e.g. evidenced by solvatochromic shifts found for some colored polyelectrolytes,[10,26,48] or by X-ray reflectograms evolving with annealing.[33] The changing arrangement of the polymers in the films might be partially due to the more and more fading influence of the support in increasingly thicker films. Still, this does not explain the marked storage effect. Strangely, the pyrene labels seem to feel a rather hydrophobic environment in fresh films which becomes increasingly polar by time, finally approaching a value similar to the one found in the aqueous solution (*cf.* Figure 3b). We have no good explanation for this so far. In any case, the observed evolution of the I_1/I_5 ratio should exclude that the polymer rearrangement is related to micro phase separation of the hydrophobic fragments, as often found in pyrene labeled systems.[49, 50]

The behavior of the hydrophobically modified polycations **3** and **4** is not unique. In a similar way, the polyanion **13** is known to form micellar aggregates in aqueous solution.[25, 51-53] Hydrophobic association in this polymer is particularly strong due to the high density of hydrophobic groups, the long alkyl spacer present, and the mesogenic character of the cyanobiphenyl residue. Nevertheless, multilayers can be prepared from polyanion **13** with a number of polycations, for instance the standard polymer **5**. The evolution of the UV/Vis spectra with the number of deposition cycles shows a linear increase of the absorbance, demonstrating reproducible, regular film growth (Figure 8). A series of previous investigations showed that the hydrophobic association of this polymer can be studied by the spectral shift of the chromophore. In the isolated form, its absorbance maximum is at 297 nm, whereas in the aggregated form, a marked hypsochromic shift is observed.[51] In fact, strong chromophore aggregation typically results in marked spectral shifts, however, whether a hypsochromic or a bathochromic shift is observed, depends on the detailed structure of the aggregates and the resulting possibilities for interaction between the chromophores.[54]

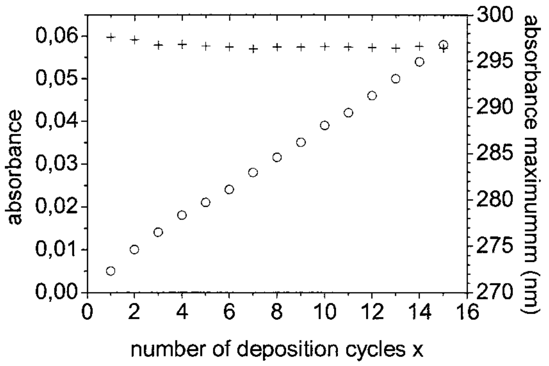


Figure 8. Growth of layer-by-layer assemblies $\{\mathbf{5}/\mathbf{13}\}_x$ followed by UV/Vis spectroscopy. (O) = absorbance, (+) = position of the absorbance maximum

In fact, aqueous solutions of polyanion **13** exhibit an absorbance band at λ_{max}= 275 nm,[25,53] indicating strong aggregation of the hydrophobic side chains. ESA multilayers $\{\mathbf{5}/\mathbf{13}\}_n$, however, have the absorbance band at λ_{max}= 296 nm (Figure 8). This indicates the dissociation of the chromophore aggregates, and the decoiling of the polyions upon adsorption. The position of the absorbance maximum is independent of the number of deposition cycles, except for the first two to three deposition cycles where a very small shift is found. Accordingly, no secondary aggregation etc. takes place in the multilayer films, as frequently observed.[10] This is noteworthy, as the functional fragments are not only strongly hydrophobic, but the 4-cyanobiphenyl moiety disposes also of a high dipole moment that would intuitively be expected to favor clustering. Though many examples of clustering of bulky, non-charged molecular fragments in ESA multilayers have been known, the here presented examples demonstrate, that clustering is not obligatory. Apparently, an appropriately chosen system may provide isolated functional fragments.

Having shown that it is a priori possible to avoid aggregation even of bulky hydrophobic groups, it would be desirable to have a rational strategy to do so on will (and not only by chance). Previous work has shown that inclusion complexation by cyclodextrins may be such a strategy.[24, 55] But this strategy is painstaking, and seems to be limited to particular molecular designs.[20] One may wonder whether the use of polyelectrolyte pairs that both dispose of bulky, but different hydrophobic substituents could minimize their aggregation in ESA films. The polarity difference between the molecular fragments in such systems is smaller, and thus the tendency for micro phase clustering and separation should be lower. In a preliminary study, we have therefore looked at the system {**6**/**13**}$_x$. Polyelectrolytes bearing azobenzene fragments, such as **6** or **7** seem to be particularly prone to aggregation in ESA films, independent whether they bear a charged moiety directly on the chromophore like **7**, or not, like **6**.[10] The ionene **6** shows an absorbance maximum at λ_{max}= 458 nm in methanol and ethanol, but at λ_{max}= 488 nm in aqueous solution. The markedly red-shifted value indicates chromophore association. As the strong absorbance of **6** at about 265 nm superposes the characteristic band of the cyanobiphenyl probe of **13** in such films, its spectral shift cannot be exploited. But the absorbance band in the visible of the azo-chromophore of **6** nevertheless is sufficiently conclusive. The absorbance maximum of films {**6**/**13**}$_x$ at about 478 nm (Table 2) demonstrates, that the use of two polyelectrolytes with hydrophobic fragments does not automatically prevent their aggregation. In fact, a decreasing content of charged groups in the polyanion seems to favour the red-shift of the band. From this point of view, the use of the overall less polar polyanion **13** poses no advantage compared to standard polyanions such as **10**. Still, we note in this system that the absorbance maximum does not shift with increasing number of deposition cycles, suggesting a stable whatsoever arrangement of the chromophores in the films.

Table 2 Position of the absorbance maximum of polycation **6** in various multilayer films

polyanion used	absorbance maximum nm	reference
poly(vinyl sulfate) **11**	443	27
poly(3-sulfopropylitaconate)	443	27
poly(3-sulfopropylmethacrylate)	468	27
poly(styrene sulfonate) **10**	478	27
13	478	this work
hectorite	498	this work
montmorillonite	500	27

An alternative strategy to prevent clustering may be the use of ionic groups on, or close to, the functional groups: the repulsion of identically charged moieties should oppose to their clustering. As discussed above, for azobenzene moieties that are known for their tendency to aggregate,[56] this approach is not successful.[10, 57] But unfortunately, even for smaller chromophores that are less prone to aggregation, such as coumarins, this strategy does not work well. This can be exemplified by the use of the coumarin functionalized, analogous polycations **8** and **9** that are mainly distinguished by their different fluorophore content. Both polycations are suited for ESA multilayer films with various polyanions. The forms of their absorbance spectra are virtually identical. The chromophore exhibits an absorbance band with a maximum in the range of 440 nm - 450 nm in solution in organic solvents, whereas for the polycations in aqueous solutions, a shoulder in the absorbance band at about 435 nm appears, suggesting some aggregation of the fluorophore for both polymers (Figure 9), similar to the behavior of polyions **3**, **4** and **13**.

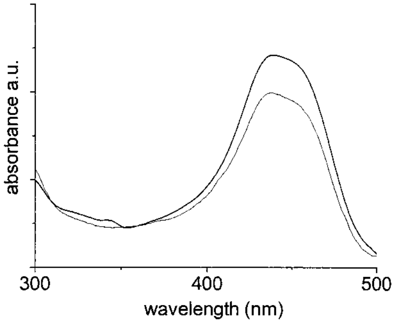


Figure 9. UV/Vis spectra of coumarin functionalized polycations **8** (top curve) and **9** (bottom curve) in aqueous solution

But different from their cases discussed above, the aggregates are not disrupted upon polymer adsorption. In the contrary, for polycation **8** with only 3 mol-% of dye, the absorbance band shifts to about 415 nm in multilayers $\{\mathbf{8/10}\}_x$, pointing to modified aggregation in the films. The extent of the spectral shift suggests the presence of aggregates of limited size (Figure 10a). Alternatively, the spectral shift might be attributed to a solvatochromic effect, though the value seems very large for the coumarin dye. The situation differs considerably for polycation **9** with the higher dye content. The complex spectrum, consisting of a broad band between 400 and 480 nm, and a strong new band at about 370 nm, indicates that the arrangement of the chromophores is not uniform in multilayers {**9/10**}$_x$. The major absorbance band at about 370 nm shows an extremely strong hypsochromic shift compared to the band of the isolated chromophore, pointing to the formation of large H-aggregates (Figure 10, curves 2 and 3).[29] The aggregation of the dye can be influenced by the choice of the solvent (Figure 10b). In fact, solvent effects were also reported for the aggregation in films of bola amphiphiles bearing oligo(thiophene)s.[40] For instance, deposition of **9** from water/DMF mixtures favors aggregate formation, as indicated by the strong hypsochromic shift of the absorbance band from about 450 nm to 375 nm. In contrast, deposition from water/isopropanol mixtures provides a spectrum similar to the one of the isolated chromophore. Accordingly, dye aggregation is efficiently suppressed. The differences found for the multilayers, however, are not reflected in the solution spectra: both mixed solvents provide spectra with the band at about 450 nm, i.e. the chromophores are isolated.

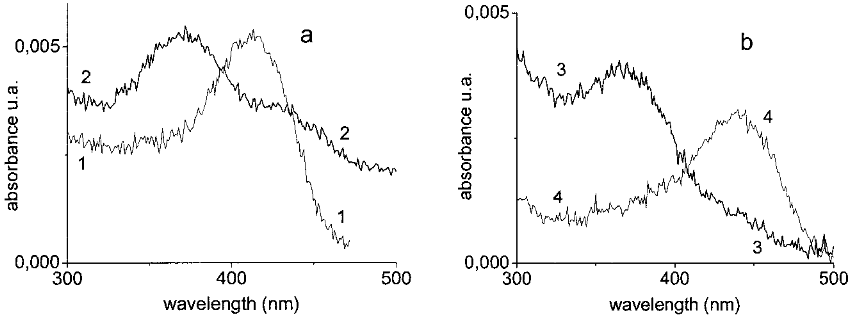


Figure 10. UV/Vis spectra of coumarin functionalized multilayer films.
a): (1) = {**8/10**}$_5$, (2) = {**9/10**}$_5$.
b): films {**9/10**}$_5$, (3) = deposited from solutions in DMF/water 1v/1v, (4) = deposited from solutions in isopropanol/water 1v/1v

This means that in one or the other way, adsorption and/or drying kinetics play a role for the aggregation of functional fragments. So far, we cannot see an intelligible relationship behind the case by case observations. The only clear effect comes form the content of functional fragments, as polycations **8** and **9** exemplify: not surprisingly, as higher the content is, the higher is the tendency for aggregation.

Conclusions

Polyelectrolyte films can be prepared from polyelectrolytes which are heavily substituted with large functional, hydrophobic fragments without particular problems. A priori, there is no need for a high charge density in the polymers. Though a strong tendency is found for many systems to form clusters and aggregates of the functional groups, it is possible to keep individual fragments isolated. This is also true for polyions with rather high contents of non-ionic fragments. In fact, experimental findings even strongly suggest that hydrophobic aggregates that are present in the solutions used for the adsorption process, can dissociate upon adsorption. The observations imply conformational transitions with complete decoiling of the polymers upon adsorption. Noteworthy, a rearrangement of chromophore fragments can still take place in the deposited films upon storage. The presence or absence of aggregates is a sensitive function of the solvent from which the polymers are adsorbed. At present, it is not possible to establish clear guidelines and rules what to do to avoid clustering/aggregation phenomena (except for dilution), - or to exploit them, respectively. Nevertheless, in the strong thrive to employ ESA films for various potential applications, one should be aware of the possible complications and pitfalls resulting from clustering or aggregation of functional molecular fragments in the films.

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