Polyelectrolytes Bearing Azobenzenes for the Functionalization of Multilayers

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SUMMARY: Thin polymeric films are assembled by the alternating adsorption of oppositely charged polyelectrolytes. The polyions are functionalized by azobenzenes, typically carrying donor-acceptor substituents. The azobenzene chromophores are exploited as versatile analytical tools, to study the assembling process, and to control the film quality. A high concentration of ionic groups does not seem to be advantageous per se for good film growth, but rather the matching of the charge densities of the polyelectrolyte pair used seems to be important. Also, the influence of the strongly interacting, form-anisotropic character of the azobenzenes on the internal film structure was investigated. Although even high concentrations of azobenzenes and of other mesogens do not induce particular ordering, a few polymer pairs allowed the construction of real multilayer films, exhibiting e.g. Bragg peaks.

Introduction

The methods to design ultrathin polymer films by self-organization have been recently complemented by the alternating physisorption of oppositely charged polyelectrolytes$^{1-4)}$. The experimental set-up of the method is simple, and the scope of useful polyelectrolytes seems to be extremely large. But up to now, little is known about the mechanism of the layer growth$^{5)}$, the limitations on the molecular level, or the detailed internal structure of the films obtained$^{1-4)}$, let alone its control. Therefore, we have synthesized and employed several series of polyelectrolytes carrying azobenzenes, as exemplified by two series of polycations **1** - **8** which are displayed in Figure 1, in order to study the build-up and the resulting structure of polyelectrolyte multilayers. The azobenzene moiety was incorporated in various ways into the polymers: it is located in the polymer main chain or in the

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side chain, fixed with and without using spacer groups, and linear as well as hyperbranched architectures were realized. The azobenzene itself may bear charged or ionizable groups, as in polymers **1** - **5** and **9**, or may be non-charged as in polymers **6** - **8**.

Such dye labeled polyelectrolytes provide numerous analytical opportunities for the study of thin films (e.g. for quantifying film growth and quality, following film formation kinetics, detect structural rearrangements, etc.). Also, the molecular characteristics of the azobenzene chromophore, for example its strongly interacting, form-anisotropic character, might be exploited to induce particular order or structures within the films.

Experimental

Materials

The water for all experiments was deionized and purified by an Elgastat Maxima system (resistance: 18.2 MΩ). 1,4-dibromo-2-butene (predominantly trans isomer), branched poly(ethyleneimine), poly{1-[4-(3-carboxy-4-hydroxyphenylazo)benzene-sulfonamido]-1,2-ethanediyl, sodium salt} **9**, poly(sodium 4-styrenesulfonate) **11**, and poly(vinyl sulfate, potassium salt) **14** were purchased from Aldrich, and were used without further purification, as was 3-aminopyridine (Fluka). N,N,N',N'-tetramethyl-1,3-propanediamine (Fluka) was distilled over CaH_2 before use. Poly-4-vinylpyridine (Aldrich) was dissolved in methanol and precipitated in hexane prior to use. The monomer 3-sulfopropylmethacrylate was a gift from the Raschig GmbH (Ludwigshafen, Germany), the monomer acrylamido-2-methylpropanesulfonate was a gift from Lubrizol (Derby, United Kingdom).

The synthesis of N,N-di-[2-(4-bromobutanoyl)-oxyethyl-]aniline, of polymer **7**, of poly(sulfopropylmethacrylate, potassium salt) **12** and of poly(2-acrylamido-2-methylpropanesulfonate, sodium salt) **13** were described before6). Polyanion **10** was prepared according to the literature7,8). The synthesis of polymer **6** is reported elsewhere9). Polymer **15** was described before10), as were **17** 11) and **19** 12). The hyperbranched polymer **5** was obtained by polycondensation of the trifunctional AB_2 monomer 3-[4'-bis-(4"-bromobutanoyloxyethyl)aminophenylazo]pyridine as described in ref.11. As this primary polymer with 50% bromine end groups is not water-soluble, it was end-capped by reacting it with a large excess of pyridine. The formed pyridinium end groups increase the density of cationic charges sufficiently to render the polymer water-soluble.

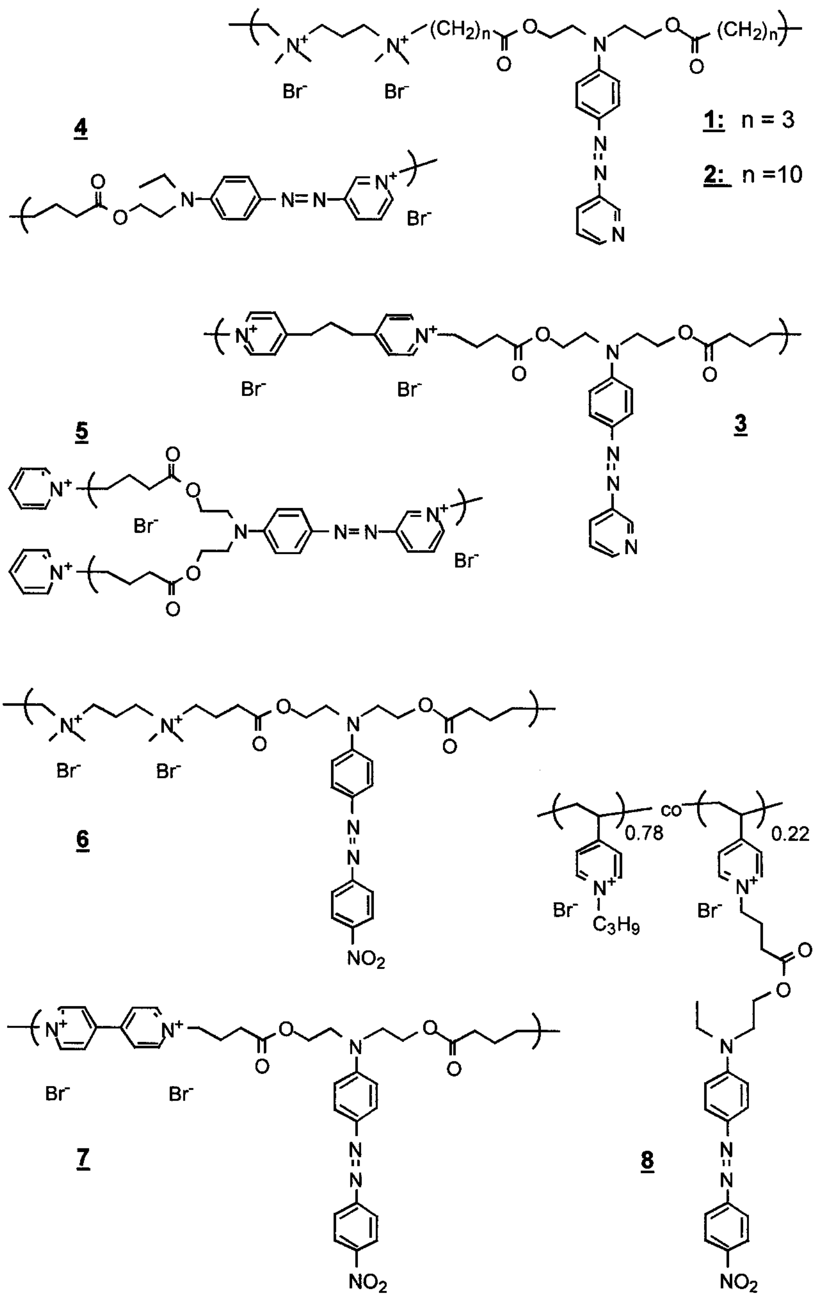


Fig. 1: polycations studied bearing azodyes.

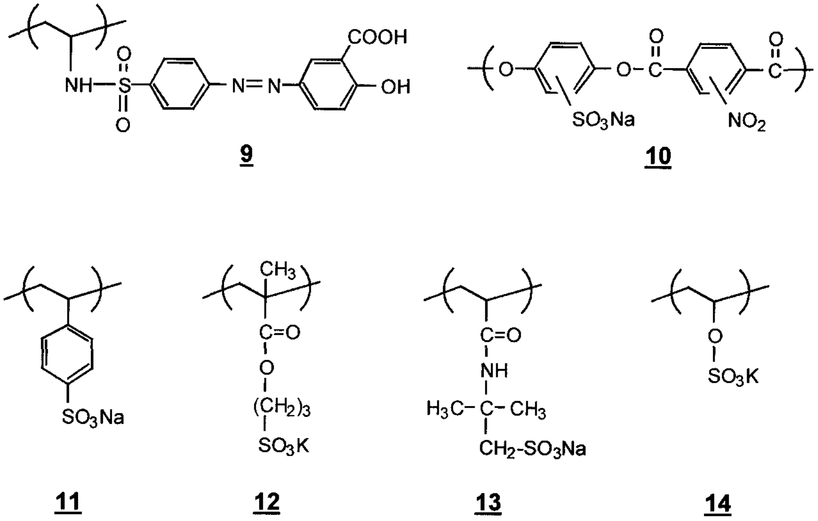


Fig. 2: polyanions employed.

Synthesis of polymer 1

77.2mg (0.82mmol) of 3-aminopyridine are dissolved in 0.9ml of 3M hydrochloric acid and cooled to 0°C. 57 mg (0.82 mmol) of $NaNO_2$ in 1.5ml of water are added dropwise while stirring. After 2h at 0°C, approximately 10mg of urea are added to destroy excess $NaNO_2$. The mixture is titrated with about 1.6ml of 0.66M aqueous $NaHCO_3$, to give pH 4-5. This solution is then added dropwise to a ice-cold solution of 250mg (0.41mmol repeat unit) of the precursor **15**[10)] in 2ml of water. The mixture is reacted for 6h while stirring in the cold, and is then allowed to reach room temperature overnight. The final mixture is precipitated into acetone, the polymer redissolved in water and lyophilized. Yield: nearly quantitative, red hygroscopic powder. For the ^{1}H-NMR spectrum, see Fig.4. According to the integration of the ^{1}H-NMR signals, the residual content of unreacted aniline moieties is negligible.

Synthesis of polymer 2

The precursor polymer which was prepared by polycondensation of N,N-bis-[2-(11-bromoundecanoyl)oxyethyl]aniline with N,N,N',N'-tetramethyl-1,3-propanediamine[9)] is coupled with diazotated 3-aminopyridine similar as described above for polymer **1**. Yield: nearly quantitative, red hygroscopic powder. According to the integration of the ^{1}H-NMR spectrum, the residual content of unreacted aniline moieties is negligible.

^{1}H-NMR (200 MHz, CD_3OD): δ[ppm] : 9.2, 9.0, 8.4, 8.2, 8.0, 7.5 (8H, =CH_{aryl}); 4.15 (2H, -COO-CH_2-); 3.60 (4H, -CH_2-N-); 3.30 (8H, -CH_2-N^+-CH_2-); 3.10 (12H, CH_3-

N^+); 2.5-2.1 (4H+2H, $-CH_2-COO$, $-N^+C-CH_2-C-N^+-$); 1.65 (4H, $-CH_2C-N^+-$); 1.2-1.55 (28H, $-(CH_2)_7-$)

Synthesis of polymer 3

0.875g (1.83mmol) of N,N-bis-[2-(4-bromobutanoyl)-oxyethyl-]aniline6) are reacted with 0.362g (1.83 mmol) of 4,4'-trimethylenedipyridine (Aldrich) in 4ml of dry dimethylformamide DMF for 7 days at 50°C under an inert atmosphere. The precursor polymer is precipitated into ethyl acetate, dissolved in water and lyophilized, to yield 1.00g (81%) of slightly yellowish powder.

^1H-NMR (200 MHz, D_2O): δ[ppm]: 8.6, 7.75 (4H+4H, $=CH_{pyridine}$); 7.05, 6.7, 6.55 (2H+2H+1H, $=CH_{aniline}$); 4.45 (4H, $-CH_2-N^+$); 4.05 (4H, $-COO-CH_2-$); 3.55 (4H, $-CH_2-N$); 2.9 (4H, aryl-CH_2-); 2.5-1.95 (10H, -aryl-C-CH_2-C-aryl, $-N^+-C-CH_2-CH_2-COO-$).

This precursor polymer is then reacted with diazotated 3-aminopyridine, isolated and purified similar as described above for polymer 1, to yield quantitatively a red, hygroscopic powder. According to the integration of the ^1H-NMR spectrum, the residual content of unreacted aniline moieties is negligible.

^1H-NMR (200 MHz, D_2O): δ[ppm] : 9.1, 8.9-8.4, 8.2, 8.0-7.4, 7.3-7.0 (1H+6H+1H +6H+2H, $=CH_{aryl}$); 4.6-4.2 (8H, $-CH_2-N^+$, $-COO-CH_2-$); 3.80 (4H, $-CH_2-N-$); 3.0 (4H, -aryl-CH_2-) 2.5-2.0 (10H, -aryl-C-CH_2-C-aryl, $-N^+-C-CH_2-CH_2-COO-$).

Synthesis of 3-[4'-(N-ethyl-N-4"-bromobutanoyloxyethyl)aminophenylazo]pyridine

2.50g (7.96mmol) of N-ethyl-N-4"-bromobutanoyloxyethyl)aniline9) are coupled with the diazonium salt of 0.75g (8.00 mmol) of 3-aminopyridine, following a standard procedure13). After the end of the reaction, the solvent is removed without heating to avoid premature polycondensation. The crude product is purified by flash chromatography (eluent: chloroform), to yield 1.1g (34%) of red oil.

^1H-NMR (200 MHz, $CDCl_3$): δ[ppm] : 9.08 (m), 8.61 (m), 8.07 (m), 7.87 (d), 7.39 (m), 6.82 (d) (1H+1H+1H+2H+1H+2H, $=CH_{aryl}$); 4.32 (t) (2H, $-COO-CH_2-$); 3.78 (t), (2H, $Br-CH_2-$); 3.4-3.6 (m) (4H, $-CH_2-N-CH_2-$); 2.50 (t) (2H, $-CH_2-COO-$); 2.15 (m) (2H, $-CH_2-C-COO-$); 1.27 (t) (3H, $N-C-CH_3$)

Synthesis of polymer 4

500mg (1.19mmol) of 3-[4'-(N-ethyl-N-4"-bromobutanoyloxyethyl)aminophenylazo}-pyridine in 2ml of dry DMF are reacted under stirring at 60°C for 72h in an inert atmosphere. Then the polymer is precipitated twice into ethyl acetate, to yield quantitatively a red solid.

^{1}H-NMR (200 MHz, DMSO-d_6): δ[ppm] : 9.6, 9.1, 8.8, 8.2, 7.9, 7.1 (1H+1H+1H +1H+2H+2H, =CH_{aryl}); 4.85 (2H, -CH_2-N^+); 4.35 (2H, -COO-CH_2-); 3.4-3.9 (-CH_2-N-CH_2-, superposed by water signal); 2.45-2.70 (-CH_2-COO-, superposed by DMSO-d_5 signal); 2.25 (2H, -CH_2-C-COO-); 1.25 (3H, N-C-CH_3)

Synthesis of 4-(N-ethyl-N-4"-bromobutanoyloxyethyl)aminophenylazo nitrobenzene

1.20g (3.82mmol) of 4-[4'-(N-ethyl-N-2-hydroxyethyl)aminophenylazo]nitrobenzene (disperse red 1) which was prepared by standard procedures13) from nitroaniline and (N-ethyl-N-2-hydroxyethyl)aniline, are reacted in 20ml of dry DMF with 0.50g (3.00mmol) of 4-bromobutyric acid and 60mg of 4-dimethylaminopyridine, and cooled to 0°C. Then 0.79 g (3.82 mmol) of dicyclohexylcarbodiimide in 20 ml of dry dichloromethane are added14). The solution is stirred at 0°C for 4h and then overnight at ambient temperature. The precipitated dicyclohexylurea is filtered off, and the solvent is evaporated. The crude product is purified by flash chromatography (eluent: $CHCl_3$), to yield 0.70 g (50%) of red oil of 4-[4'-(N-ethyl-N-4"-bromobutanoyloxyethyl)aminophenylazo]nitrobenzene.

^{1}H-NMR (200 MHz, $CDCl_3$): δ [ppm] : 8.3 (d), 7.9 (m), 6.8 (d) (2H+4H+2H, =CH_{aryl}); 4.3 (t) (2H, -CH_2-OOC); 3.8 -3.4 (m) (6H, Br-CH_2-, -CH_2-N-CH_2-); 2.5 (t) (2H, -CH_2-COO-); 2.1 (m) (2H, Br-C-CH_2-C-COO-); 1.2 (t) (3H, N-C-CH_3)

Synthesis of polymer <u>**8**</u>

In analogy to ref.15, 200mg (1.90mmol) of poly-4-vinylpyridine and 400mg (0.86 mmol) of azo dye 4-[4'-(N-ethyl-N-4"-bromobutanoyloxyethyl)aminophenylazo]nitrobenzene are stirred in a mixture of 9 ml of ethanol and 9ml of nitroethane for 48h at 70°C. Then 2.0ml (ρ=1.352g/ml, 21.97mmol) of 1-bromopropane are added, and the reaction is continued for 48h. The solvent is evaporated, the polymer is dissolved in methanol, precipitated into ether, redissolved in water, and lyophilized, to yield 500 mg (89%) of dark red, hygroscopic powder. The ^{1}H-NMR spectrum indicates close to quantitative quaternization of the pyridine groups. The integration gives a ratio x:y of 78:22 for repeat units quaternized by propyl residues to such which are functionalized by the azo dye.

^{1}H-NMR (200 MHz, D_2O): δ [ppm] : 8.9-8.2, 8.0-7.1 (=CH_{aryl}); 4.6-4.2 (-N^+-CH_2, -COO-CH_2); 3.0-1.5 (-CH_2-N-CH_2-, N^+-C-CH_2-, -CH_2-COO-, -CH_2-$CH_{\text{-backbone}}$); 1.1 (N-C-CH_3); 0.9 (N^+-C-C-CH_3)

Synthesis of polymer <u>**16**</u>

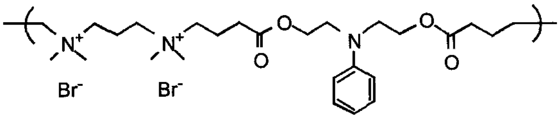
1.371g (6.409mmol) of 1,4-dibromo-2-butene and 1.000g (6.402mmol) of 4,4'-bipyridine in 8ml of dry DMF are reacted at ambient temperature for 48h. The mixture is repeatedly precipitated into a 1v/1v mixture of $CHCl_3$/methanol, finally dissolved in water and lyophilized, to yield nearly quantitatively a white, hygroscopic powder.

^{1}H-NMR (200 MHz, D_2O): δ[ppm] : 9.12 (d), 8.55 (d) (4H+4H =CH_{aryl}); 6.44 (s, broad); (2H, =CH-); 5.45 (s, broad) (4H, -CH_2-N^+)

Synthesis of polymer ***18***

N,N-bis-1,6-(4-bromobutanoyloxy)-hexane was prepared by a standard procedure$^{14)}$ from 1,6-hexanediol and 4-bromobutyric acid. 0.500g (1.20mmol) of bis-1,6-(4-bromobutanoyloxy)-hexane are reacted with 0.238g (1.20mmol) of 4,4'-trimethylenedipyridine (Aldrich) in 4ml of dry DMF for 7 days at 50°C under an inert atmosphere. The polymer is repeatedly precipitated into ethyl acetate, finally dissolved in water and lyophilized, to yield 0.38g (51%) of white powder.

^{1}H-NMR (200 MHz, D_2O): δ[ppm] : 8.75, 7.95 (4H+4H, =CH_{aryl}); 4.6 (4H, -CH_2-N^+); 4.05 (4H, -COO-CH_2-); 3.05 (4H, aryl-CH_2-); 2.5-2.05 (10H, -aryl-C-CH_2-C-aryl, -N^+-C-CH_2-CH_2-COO-), 1.6, 1.3 (4H+4H, O-C-$(CH_2)_4$-C-O).



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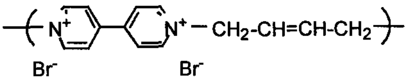

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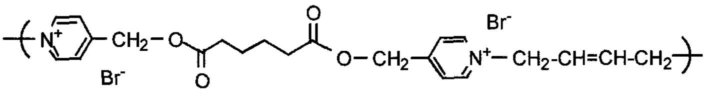

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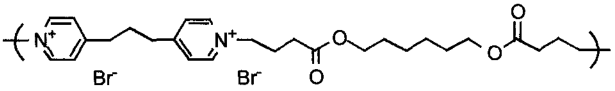

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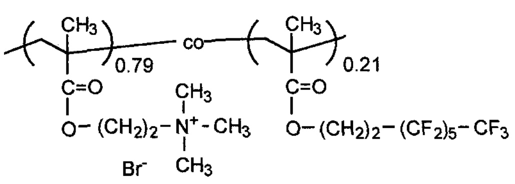

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Fig. 3: non-coloured polycations employed.

Preparation of the layer-by-layer assemblies

Float glass plates, suprasil quartz plates and silicon wafers were used as supports for the layer-by-layer assemblies. They were treated as described in ref.16 to clean them and to create a negatively charged surface allowing for the first adsorption step. If not mentioned otherwise, an initial buffer layer of poly(ethyleneimine) and poly(vinyl sulfate) **14** was deposited onto all supports, prior to subsequent adsorption steps of the various polyions.

For the layer-by-layer assembly, the polyions were dissolved in ultra-pure water with a concentration of $2 \cdot 10^{-2}$ mol l^{-1}, based on the polymer fixed charges. Exceptionally, polycations **1** - **3** were dissolved in 0.1M HCl. The layer-by-layer assemblies were prepared by alternating dipping of the supports into a polycation solution and a polyanion solution for 20min, if not stated otherwise. Before changing the solution, the supports were dipped subsequently into three beakers with ultra-pure water for 30s each in order to remove adhering excess solution.

Instruments

NMR spectra were taken with a Gemini-200 spectrometer from Varian. The UV/VIS spectra were recorded with a DW 2000 from SLM-AMINCO. Infrared spectra were performed with a 1710 Infrared Fourier Transform Spectrometer (Perkin-Elmer). The X-ray facilities were described in detail elsewhere17).

Results and Discussion

Synthetic strategies towards azobenzene functionalized polyelectrolytes

The polycations bearing azobenzene chromophores which were investigated are displayed in Fig.1. The substituents of the azobenzene moiety were chosen such to provide intense colour in the visible. In consequence, these polycations are strongly orange to red coloured. The polyanions used are shown in Fig.2. They are typically colourless, with the exception of the azobenzene carrying polymer **9**. Some non-coloured polycations which were employed are listed in Fig.3

As far as possible, the various polyelectrolytes were prepared in one step from the appropriate monomers. One route was the free radical polymerization of charged vinylic monomers, placing the charged groups into the side chain. The alternative route used polycondensation of dibromides with tertiary diamines to obtain polymers with ammonium groups in the main chain, the so-called ionenes. In these ways, the chemically best defined polymers are obtained. Only if the azobenzene fragments were not compatible with the polyreaction, as was the case for 1 - 3 and 8, the polymers were prepared by modification of appropriate precursor polymers. In the case of 1 - 3, direct polycondensation of e.g. 3-[4'-bis-(4"-bromobutanoyloxyethyl)aminophenylazo]pyridine with the diamine would lead to crosslinked products (cf. the synthesis of the hyperbranched polycation 5). In the case of 8, the nitroazobenzene moiety is strongly retarding or even inhibiting free radical polymerization. As illustrated by the ^{1}H-NMR-spectrum of polymer 1 in Fig.4, the chemical modification by azo coupling allows nearly complete functionalization of the reactive moieties of the precursor polymers. The presence of the ammonium groups in the polymer backbone allows to dissolve polymers 1 - 3 at acidic as well as at neutral pH in water, i.e. the protonation of the pyridine fragment is not obligatory for water-solubility.

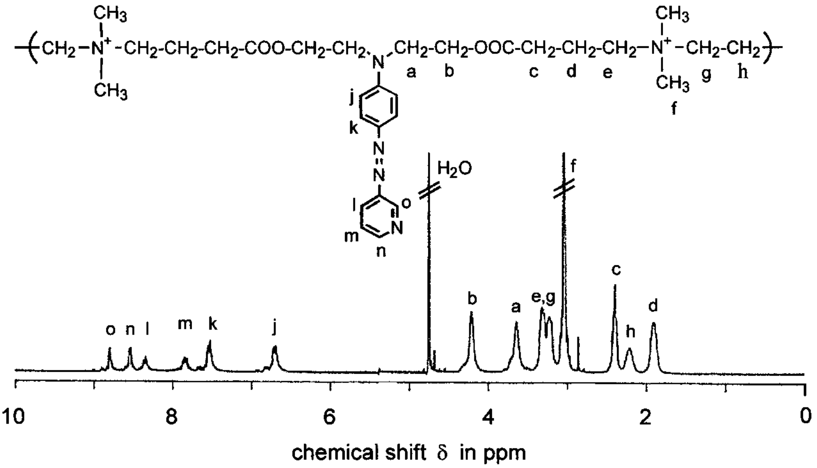

Fig. 4: ^{1}H-NMR-spectrum of polymer 1 in D_2O.

Use of azobenzene functionalized polyelectrolytes for the construction of layer-by-layer assemblies

Use of the colouration

The inherent strong colour of the azobenzene functionalized polyelectrolytes is already as such a very useful tool for model studies. It provides in the simplest case an easy means to analyze the build-up of the thin films on the substrates by following the evolution of the absorbance with increasing number of adsorption steps. A particular advantage of the optical spectroscopy is that no critical assumptions on the nature of the support need to be made, different from ellipsometry for example. Further, the evolution of colour enables to verify the overall homogeneity of the films by the naked eye or - more elaborately - by an optical microscope. These fundamental information, combining large scale survey and small scale evaluation (with optical resolution), are not trivial to obtain otherwise, in particular as we are dealing typically with film thicknesses in the nm range. Also, the colour based quality control is rapid, non-destructive, quantitative and does not require expensive equipment. Of course for a detailed analysis, the optical evaluation of the film quality must be followed by more complex analytical methods of higher resolution, such as electron microscopy or atomic force microscopy.

In addition, the colour of the layer-by-layer assemblies facilitates numerous investigations of the final coatings, e.g. on their stability against mechanical stress or against solvents, as any removal of material is rapidly detected11). E.g. when applying a scotch tape test, we have found in general that neither colour is removed from the samples, nor coloured material is transferred to the adhesive tape. This demonstrates the good adhesion of the assemblies to polar substrates such as glass or quartz. Also, alternating polyelectrolyte films are typically inert towards dissolution by organic solvents. On the contrary, assemblies prepared on hydrophobic supports such as untreated polymers like polypropylene adhere very poorly only, therefore requiring special treatment such as photocuring11).

For the vast majority of azobenzene functionalized polyelectrolytes - as exemplified in Fig.1 or by polyanion **9** -, we have observed the formation of coherent and homogeneous coatings, as indicated by their uniform colouration. This is true for most other dye functionalized polyions we have studied, too. The uniform colouration is independent of whether the chromophore bears an ionic group itself (cf. (protonated) polymers **1** - **5** and **9**), or not (cf. polymers **6** - **8**), and whether the density of ionic groups in the polymers is high or not. Also, various polymer architectures and complex substitutions are permitted. Uniform coatings are even obtained if film growth is not linear (see below). Therefore we can conclude that the layer-by-layer assembly of polyelectrolytes is, at least at the level of optical resolution, generally a little demanding, extremely versatile method to obtain uniform coatings.

Quantification of film growth by UV/VIS spectroscopy

Compared to the generally found lateral uniformity of the coatings, the uniformity of film growth is less evident. Often, film growth starts rather sluggishly for the first adsorption steps, until marked growth is seen (cf. Figs.5, 6, 8). The difficulties in depositing the first layers are attributed to the rather low charge density of the support, so that a certain number of adsorption cycles is needed until the complexation of the polyions at the surface is in equilibrium18,19).

But even for thicker films, growth is not necessarily linear. Only in favorable cases, linear growth with the number of adsorption cycles is achieved. This is the case for many standard polyelectrolytes, i.e. such with high charge density, in particular when using intermediate ionic strengths20). At low or high ionic strengths however, or when using polyions of low charge density, severe difficulties can be encountered. Often, a critical minimum charge density is invoked for obtaining regular film growth17,20,21). This implies inherent difficulties when functionalized polyelectrolytes are employed, e.g. when incorporating the rather big and hydrophobic azobenzene moiety.

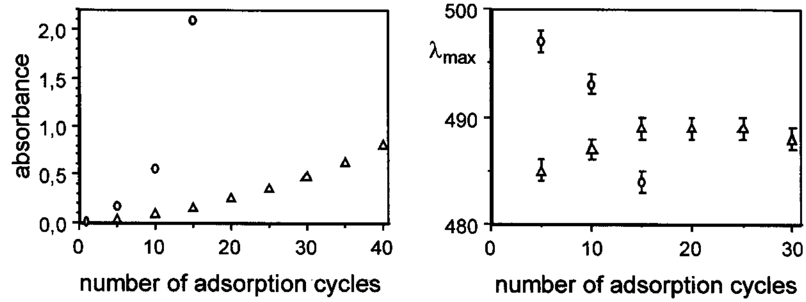

Fig. 5: growth of layer-by-layer assemblies on quartz made from polyanion <u>13</u> with linear polycation <u>4</u> (o), or with its hyperbranched analogue <u>5</u> (Δ) respectively. Left: evolution of the maximum absorbance, right: evolution of λ_{max}.

This problem is exemplified in Fig.5 for assemblies made of polymers <u>4</u> and <u>5</u> with the standard polyanion <u>13</u>. In the case of the linear analogue <u>4</u> in which the few charged sites are localized only on the azobenzenes, the growth is pseudo-exponential. Presumably, no efficient decoiling takes place during the adsorption and big, non-coherent patches of polymer are adsorbed[21]). The resulting surfaces become increasingly rough, thus leading to a pseudo-exponential increase of adsorbed material for not too high numbers of adsorption cycles. Interestingly, a marked spectral shift of the absorbance band is observed, which will be discussed later. If however the charge density is increased, as for the hyperbranched analog 5 due to the numerous additional pyridinium end groups, continuous linear film growth is obtained.

Instead of pseudo-exponential growth, low charge densities may lead to asymptotic growth, too, as illustrated in Fig.6 for the analogous polycations 3 and 18 adsorbed with polyanion 11. In the case of 3, the azobenzene chromophore provides additional charge density when protonated. This modification allows regular growth, different from the unmodified analogous ionene 18.

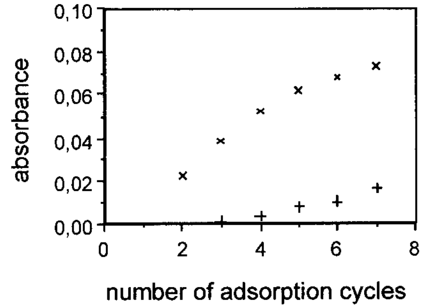

Fig. 6: growth of layer-by-layer assemblies on quartz made from polyanion 11 and polycation 3 (+, λ_{max}=446nm), or its analogue 18 without azobenzene group (x, λ_{max}=226nm).

But even so, polycation 3 seems to be a limiting case for good deposition. Whereas the alternating deposition of 3 with the somewhat hydrophobic poly(styrenesulfonate) 11 allows regular growth, this is not true for the densely charged polymethacrylate 12. This is in contrast to the more hydrophilic analogues 1 and 2, which allow good multilayer build-up even with the very hydrophilic polyanion poly(vinyl sulfate) 14 (cf. Fig.8)

A similar observation is made for polycation 7 which has a low charge density, too. Assemblies of 7 with the rather hydrophobic 11 grow regularly, whereas irregular growth takes place with densely charged polyanions such as **12**, **13** or **14** 6). Obviously, high charge densities are not necessarily favorable for successful deposition; the right combination of polyanion and polycation is important.

The observed selectivities may be related to matching or not matching charge densities, keeping in mind that the final layer-by-layer assemblies usually do not contain low molar mass counter-ions[22,23]. A large mismatch would leave many ionic groups of the densely charged polyion unpaired. Alternatively, additional interactions than electrostatic ones may be invoked, such as hydrophobic or π-π interactions. Otherwise, the successful alternating deposition of some liquid crystalline ionomers carrying bulky azobenzene mesogens are difficult to explain, as they contain only about 1 ionic group per 100 atoms[24,25].

Not surprisingly, the problem of matching polyion pairs is encountered for azobenzene functionalized polyanions, too. Polymer **9** allows regular layer build-up with so strongly varying polycations such as **5**, **16** and **19**, but not with **15** or **17** (Fig.7). (Additionally, substantial spectral differences and shifts are observed, which will be discussed below). Nevertheless, the intermediate charge density of this polymer, together with the possible additional interactions such as H-bonding, hydrophobic interactions or π-π ones could explain the versatile usefulness of this particular polyanion in the past[11, 26-29]: a marked mismatch is not to be expected with most polycations.

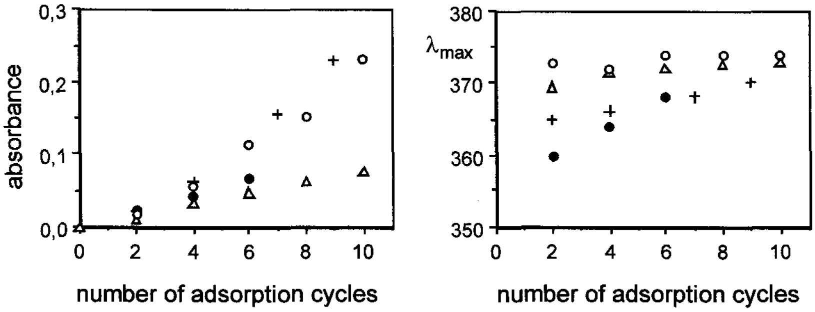

Fig. 7: growth of layer-by-layer assemblies on quartz made from azobenzene bearing polyanion **9** and polycations **15** (o), **16** (Δ), **17** (+), and **19** (•).
Left: evolution of the maximum absorbance, right: evolution of λ_{max}.

Kinetics of polyelectrolyte adsorption

In general, adsorption periods of 15min-20min are applied for polyelectrolyte adsorption, under the assumption that the saturation value has been reached. In fact, there are a number of studies on the kinetics of polyion adsorption, using so different methods like Quartz Crystal Microbalance QCM[30)], radiolabeling[31,32)], reflectometry[20,33)], ellipsometry[34)], Surface Plasmon Resonance SPR[27)], X-ray photoelectron spectroscopy XPS[19)], or atomic force microscopy AFM[35,36)]. Typically saturation is reached after 5-60 min; most frequently 10 min - 20 min periods are found. Still, it must be kept in mind that the adsorption kinetics depend sensitively on ionic strength and pH of the solution, as well as on the molar mass of the polyelectrolyte[20)].

Coloured polyelectrolytes are natural candidates for kinetic studies without the need for complicated equipment, since the absorbance enables the facile quantification of the adsorbed material. Early studies on poly(thiophene-3-acetic acid) found saturation after about 10min[37)]. Comparable adsorption rates were reported most recently for some charged, azobenzene modified epoxy resins[38)].

However, these findings cannot be generalized. The adsorption process is for example somewhat slower for films made of polycation **2** and polyanion **14**. Such assemblies require about 60min to reach the adsorption plateau at pH=1 (Fig.8a). The adsorption process is extremely rapid in the beginning, then slowing down gradually. After about 60min, the absorbance seems to converge to a plateau value. Nevertheless, prolonged studies over several days show that small additional quantities of **2** are still slowly adsorbed. Clearly, the generally accepted adsorption periods of 15-20min are not always sufficient, and should be verified for each case.

Remarkably, much shorter adsorption times than needed to approach the saturation value can be applied to prepare regular layer-by-layer assemblies. This means that partial monolayer coverage may suffice for continuous film growth. For example, only 1min of exposure to solutions of **2** is sufficient to enable linear growth of the absorbance with the number of adsorption cycles (Fig.8b).

Although periods of 10 min -30 min of adsorption seem to be needed in most cases to reach saturation, much shorter times may suffice in special cases. For example, the adsorption of polycation **8** on a layer of polyanion **14** achieves saturation in less than 1min. As found for **2**, such rapid adsorption steps do not interfere with linear film growth, which is shown by the linear increase in absorbance with the number of adsorption cycles (Fig.8b)

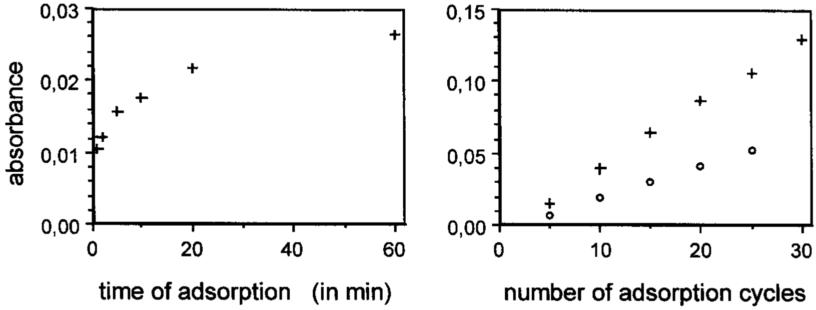

Fig. 8: growth of layer-by-layer assemblies of azobenzene functionalized polycations with poly(vinylsulfate) 14 on quartz, followed by the absorbance at 485nm.
a) kinetics of the adsorption of 2 on a primer bilayer made of poly(ethyleneimine) and 14. b) film growth for 1min adsorption time: (+) = 2, (o) = 8.

Similar fast adsorption close to the diffusion limit was reported recently for silica and poly(diallyldimethylammonium chloride)39,40). Obviously, the adsorption kinetics of polyelectrolytes depends strongly on the detailed chemical structure of the polyion pair used; if properly chosen, the process can be extremely fast.

Metachromic effects in layer-by-layer assemblies

The absorbance spectrum of azobenzene chromophores depends sensitively on the specific environment and on aggregation41). Therefore, azobenzenes may serve as convenient probes for structural studies of polyelectrolyte films. Strong spectral differences with changing environment are typically expected for donor-acceptor substituted azobenzenes as found in polycations 6 - 8 with amino and nitro substituents, and to a lesser degree in the chromophore of polycations 1 - 5. In fact, polycation 6 shows a marked shift of its absorbance spectra in dependence on the polyanion chosen6). The comparison of assemblies from polyanion 13 with the linear polycation 4 or with its hyperbranched analogue 5, respectively, demonstrates that even the use of the same chromophore in the basically same chemical structure (except for the topology) with the same polyion does not produce identical results (Fig.5). Also, marked spectral variations have been reported for layer-by-layer assemblies of polyanion **9**, whose absorbance maximum in water is at λ_{max} = 362nm. Assemblies with poly(diallyldimethyl ammonium chloride) exhibit λ_{max} = 390nm, with poly(ethyleneimine) λ_{max} = 380nm, and with poly(3-(N-ethyl-N,N-dimethyl)ammoniopropylmethacrylamide) λ_{max} = 372nm[28,29]. The additional examples displayed in Figs.7 and 11 illustrate the diversity encountered. Although a detailed evaluation of the reported spectral variations is not possible due to the scarcity of structural data which could be correlated, the differences in the position of the absorbance maxima are striking.

The strongly changing environment of the chromophores, in dependence on the oppositely charged polyelectrolyte partner chosen, fits well with the model of at least partial interpenetration of the polycation and polyanion "layer"[1,2], as otherwise thicker layers should display characteristic absorbance maxima. Still, the spectral differences observed seem to have more implications. A remarkable feature is the frequently encountered shift of the absorbance maximum with increasing number of adsorption cycles (cf. Figs. 5, 7 and 11). Very strong spectral shifts seem to be found for irregular growth. But the phenomenon may appear for regular growth as well[29]. A particular marked case is illustrated in Fig.9, for fast grown films from **2** and **14**.

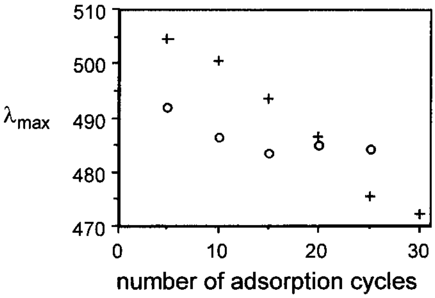

Fig. 9: Spectral shift in layer-by-layer assemblies on quartz of poly(vinyl sulfate) **14** with polycation **2** (+), or with polycation **8** (o); adsorption time = 1min.

The absorbance maximum shifts continuously from 505 nm for an assembly after 5 adsorption cycles to 475 nm for an assembly after 30 cycles. This result contrasts with assemblies of the same system grown with 20min time for each adsorption step[42], where the absorbance maximum of about 487nm hardly changes with the number of assembly steps. However, the strong metachromic effect is not just a consequence of the short adsorption step, but seems rather to be specific for this system. For identically fast grown assemblies of **8** with **14** e.g., the absorbance maximum shifts only weakly with the number of adsorption cycles from 492nm to 485nm within the first deposited layers.

The continuous spectral shifts with ongoing film growth imply a change of the internal structure of the newly deposited polyelectrolyte layer. But as a shift and not a mere broadening of the absorbance bands is observed, they suggest even a rearrangement of the chromophores allover the film. Either the interactions among polycations and polyanions are different in thicker layers, or the chromophores are aggregating in a different way. This phenomenon is not understood. As spectral shifts are often most notable during the first deposition cycles (cf. Figs.5 and 7, or ref. 29), the phenomenon might be related to the initial sluggish growth until equilibration is obtained (see above). In any case, it demonstrates that polyelectrolyte films are not static structures, but are subject to dynamical processes29). This is not surprising keeping the hydrogel character of the films in mind, and their sensitivity to changes in humidity26,43).

Induction of structure in layer-by-layer assemblies of azobenzene functionalized polyelectrolytes

Polyelectrolyte layer-by-layer assemblies are normally amorphous and not structured.1-4). This is attributed to the strong interpenetration of the oppositely charged polyions in the final films1,2). Scattering techniques for example do not reveal defined sublayer formation - in contrast analogous to smectic liquid crystalline phases or Langmuir-Blodgett films - except for when applying particular physical treatments. Examples are patterned drying periods26), or the incorporation of selectively deuterated layers for neutron scattering2). Otherwise, Bragg peaks indicating sublayer formation required the presence of preformed lamellar layers, e.g. from Langmuir-Blodgett-type interlayers44) or from bola amphiphiles45,46). The few exceptions from this lack of internal structure are based on the use of extremely form-anisotropic, rigid polyelectrolytes such as very large smectite clay particles, graphite oxide, or exfoliated phosphates47-50).

Within this line, we wondered whether the azobenzene moiety would be useful to induce substructures into layer-by-layer assemblies of polyelectrolytes. The stiffness, the hydrophobicity, the strong π-π interactions, and the form anisotropy of azobenzenes are known to render them to useful building blocks to induce order in various polymer systems, e.g. leading to liquid crystallinity51). This tendency of the azobenzene group is so strong, that particular ordering effects are observed in a number of self-organized structures, such as Langmuir-Blodgett Films, or in vesicles and lamellar lipid bilayers41,52).

Ordering due to the azobenzene fragments could result in two distinct effects. Either order is induced within the plane of the deposited layers if the azobenzenes lie flat on the support and are preferentially aligned in one direction, ("2D-nematic order"). Or an ordered sequence of well distinguished sublayers is created if the azobenzenes are preferentially aligned normal to the support, like in smectic liquid crystals as schemed out in Fig.10.

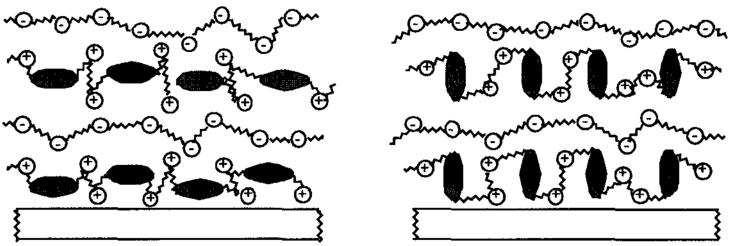

Fig. 10: model for some possible liquid crystalline alignments of calamitic mesogens in polyelectrolyte layer-by-layer assemblies: left nematic arrangement parallel to the support. right: smectic arrangement normal to the support.

Concerning the induction of order within the plane of layers, no birefringence has been observed so far in all of our systems containing azobenzene functionalized polyelectrolytes. Also, spectra taken with linearly polarized light have not shown a preferred orientation of the chromophores in the plane of the films. The lack of order is not just a result of the dilution of the azobenzenes, as assemblies built from two polyelectrolytes with azobenzene groups or with mesogenic units do not yield different results. Neither the combination of **5** and **9**, of **5** and **10**, or of **9** and **16** results in in-plane order, although the polyions **10** and **16** are known to display lyotropic liquid crystalline behaviour[8,53].

Concerning the induction of smectic like structures, the situation is less clear. Generally in scattering experiments, no Bragg reflections are found for films made from azobenzene containing polyelectrolytes. Again, the lack of order cannot be attributed to a dilution of the azobenzenes. Assemblies built from two polyelectrolytes with azobenzenes or mesogenic units - such as the combination **5** / **9**, of **5** / **10**, or **9** / **16** - do not behave differently from "mixed" assemblies made with only one mesogen modified polyelectrolyte[24,25]. In fact, as Fig.11 exemplifies with the system **5** / **10**, these combinations do not even yield fully regular linear growth in all cases. It seems, that the tendency of the azobenzene moieties to self-organize a priori cannot compete with the interfering pairing of oppositely charged ionic groups.

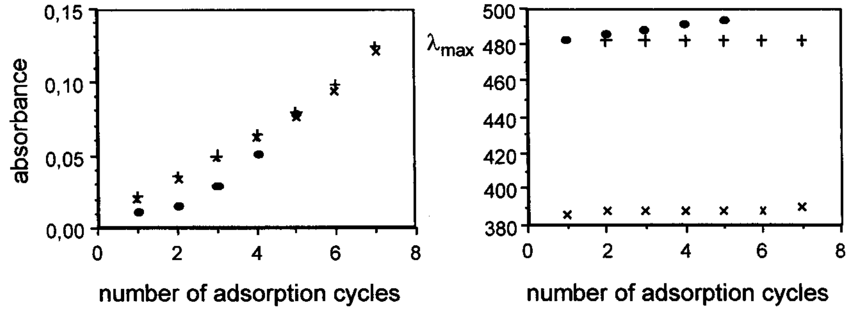

Fig. 11: growth of layer-by-layer assemblies on quartz made from hyperbranched polycation 5 and complex polyanions.

Left: evolution of the absorbance: assemblies of 5 and polyanion 9 followed by the band at 390nm (x, characteristic for 9) and at 480nm (+, characteristic for 5). Assemblies of 5 and 10 followed by the absorbance at 490nm (•).

Right: evolution of λ_{max}, same symbols.

Nevertheless, we found that in exceptional cases multilayers with a defined lamellar substructure occur$^{17,42)}$. Assemblies of polycations 2 or 6 with the standard polyanion 14 exhibit several orders of Bragg peaks in X-ray reflectograms (Fig.12).

The thicknesses of the individual layers are calculated to be 2.42nm and 2.43nm, respectively. This internal sublattice is extremely sensitive to the detailed molecular structure of the azobenzene carrying polyion. Whereas assemblies of 14 with 2 and 6 show Bragg peaks, the ones made with the closely related analogues 1 and 7 do not. The polyanion used plays a crucial role, too: Bragg peaks are absent in films of 2 and 6 when polyanions 11 or 13 are employed instead of 14. Nevertheless, the above presented examples demonstrate that polyelectrolyte assemblies can dispose of an internal structure. Therefore, they may be useful even in a larger context than supposed up to now, thus challenging domains which were so far thought to be reserved to Langmuir-Blodgett films or self-assembled multilayers$^{4)}$.

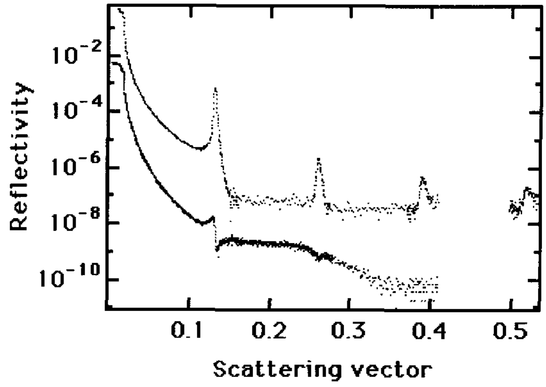

Fig. 12: X-ray reflectrograms of multilayers made with polyanion 14 on Si-wafers (20 adsorption cycles). Top: using polycation 2; bottom: using polycation 6.

The formation of sublayers in the layer-by-layer assemblies for particular cases requires a preferential alignment of the azobenzene chromophores. If preferential alignment can be extended to preferential orientation, the use of dichroic dyes such as in polycations 6 - 8 would give access to coatings useful for second-order non-linear optical (NLO) applications[54]. Indeed most recently, occasional reports indicated a preferential orientation of azodyes for the first adsorbed layers[6,28,38,55]. But beyond 3 to 5 adsorption cycles, the orientational effect seems to fade away. This suggests an ordering effect due to the surface of the support, and not inherent to the adsorption process as such. Such an explanation would be coherent with the influence of the support on beginning film growth, which often becomes regular only after 4-6 adsorption cycles (cf. discussion above). Therefore, it seems that more complex strategies will be needed[56-58], if NLO-properties of azodyes shall be exploited in layer-by-layer assemblies of polyelectrolytes.

Reactive layer-by-layer assemblies

One of the strategies to obtain functional polyelectrolytes bearing azobenzenes used the modification of precursor polymers, which are reactive towards diazonium salts, such as polycation 15. The stability of the layer-by-layer assemblies allows to apply such post-modifications in-situ, in the preassembled films, too. The few present studies[9,29] of in-situ azo coupling demonstrate the feasibility of this approach, and the permeability of the diazonium salts deep into inner layers. This implies on the one hand, that efficient functionalization can be achieved throughout the films, possibly realizing a gradient. On the other hand, this strategy does not seem to allow a facile, exclusive modification of the topmost layer; i.e. a selective chemical surface functionalization will be difficult.

A very particular case is the preparation of layer-by-layer assemblies by combining the adsorption of reactive polyelectrolytes on charged surfaces, followed by an activation reaction to induce charge reversal at the surface (coatings by multiple polyelectrolyte adsorption / surface activation CoMPAS)57). In-situ azo coupling of sulfonated diazonium salts on polycations such as <u>**15**</u> is well suited for this strategy, and provides good results10,56,57). The CoMPAS process does not only introduce additional versatility to the standard adsorption procedure for layer-by-layer assemblies, but allows in particular to create oriented, non-centrosymmetric structures, which are e.g. presenting non-linear optical effects56,57).

A special feature of azobenzenes is the reversible trans-cis photoisomerization. So far, no examples have been reported for polyelectrolyte bound azobenzenes in layer-by-layer assemblies, but first reports exist on low molar mass azodyes59). For sure, this interesting field will be followed up in the near future.

Conclusions

A number of azo dye containing polyions with different molecular architectures were synthesized. Despite of their diversity, they can be successfully employed for the assembly of polymeric films by the alternating adsorption with oppositely charged polyelectrolytes. The azobenzene chromophores are versatile analytical tools, to study film growth, the kinetics of the assembling process, to control the film quality, or to detect subtle structural changes within the films. Saturation in the adsorption isotherms of the polyions can vary from seconds to hours, depending on the system. Incomplete adsorption layers obtained after only short adsorption periods, may allow regular layer-by-layer growth nevertheless. A high concentration of ionic groups seems neither to be necessary, nor per se to be advantageous for good film growth. Rather, the matching of the charge densities of the polyelectrolyte pair used seems to be important. Though azobenzenes are known to interact strongly, no general particular ordering effect was observed in the polyelectrolyte films. Only in very special cases and when combined with the appropriate partner polyion, the functionalized polymers allowed the construction of real multilayer films, exhibiting e.g. Bragg peaks.

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