Macromol. Symp. **126,** *105–121 (1997)*

MULTILAYERS BY ADSORPTION OF FUNCTIONAL POLYELECTROLYTES

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Abstract: The synthesis of polycations bearing reactive groups, namely tertiary anilines located in the side chain or in the main chain, is described. These polyions are employed in conventional alternating polyelectrolyte multilayer assembly or in a modified build-up process including an azo coupling reaction on the topmost layer after every polycation adsorption step, which offers the potential to create multilayer structures with a non-centrosymmetric structure. The characterization of these modified assemblies by UV/VIS spectroscopy reveals significant differences in the spectral data in dependence of the polycation structure.

INTRODUCTION

The assembly of defined multilayers by alternating polyelectrolyte adsorption (Ref. 1) is a convenient and versatile method for the modification of surfaces of virtually any size and shape. It is relatively fast and does not require expensive equipment. Moreover, a wide variety of polyions bearing functional groups can be employed for the technique, such as polymers bearing conducting moieties (Ref. 2), photoluminescent groups (Ref. 3), dye moieties (Ref. 4) or groups for molecular recognition, comprising natural polymers such as DNA (Ref. 5) or synthetic polymers (Ref. 6).

In addition, it is not only possible to deposit the polyelectrolytes as such, but to modify them as well by chemical reactions after deposition. This seems to be an interesting alternative, because compared to other thin films obtained by self-organization methods, such as Langmuir-Blodgett films, there should be a smaller risk of damaging the layered structures by such a reaction. Polyelectrolyte multilayers are a priori less ordered assemblies and should thus be less prone to destructive structural rearrangements in the course of a chemical reaction. Also, the less dense structure should enable the diffusion of small molecules into the assembly. Still, it is not clear whether, and if so to which extent, the steric restrictions etc. will interfere or modify the chemical reactivity in such thin films. Up to now, there are only few examples for the reactive modification of polyelectrolyte multilayers: the creation of conjugated structures by elimination in polycations (Ref. 7), the cyclization of poly(amic acids) to

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polyimides (Ref. 8) and the photocrosslinking of polycations bearing styrenic groups (Ref. 9). But all these reactions take place without the participation of a reagent from outside of the assembly.

We have therefore explored the chemical modification of polyelectrolyte multilayers by reaction with small molecules approaching from the outside. For this purpose we chose an azo coupling reaction since the evolution of colour allows to monitor the progress of the reaction easily, and to judge the overall quality of the modified assemblies by the bare eye.

The polycations investigated carry reactive tertiary aniline groups. The modification of the polycations on the layer is done by azo coupling with the diazonium salt of 4-nitroaniline. In order to study the influence of the molecular architecture on the multilayer assemblies, we chose the ionene-type polycation **1** with the reactive group directly attached to the polymer backbone, and the copolymer **2** in which the reactive group is placed in the side-chain, separated from the main chain by a flexible spacer.

RESULTS AND DISCUSSION

Synthesis of the Polymers

The polymers employed for the study were synthesized by standard procedures. The synthesis of poly(sulfopropyl)methacrylate **3** is reported in ref. 10. The chemical formulae of the polymers are shown in figure 1.

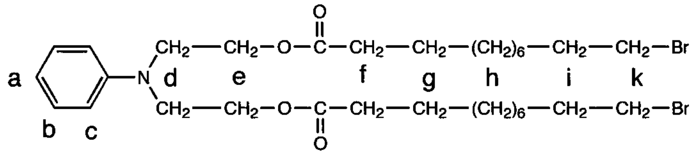
Synthesis of N, N-di-[2-(11-bromoundecanoyl)-oxyethyl-]aniline

In analogy to the procedure of Neises and Steglich (Ref. 11), 3.00 g (16.55 mmol) of N-phenyldiethanolamine, 9.65 g of 11-bromoundecanoic acid and 80 mg of 4-dimethylaminopyridine (DMAP) are dissolved in 70 ml of dry dichloromethane and cooled to 0°C. Then a solution of 8.26 g of dicyclohexylcarbodiimide (DCC) in 30 ml of dry dichloromethane is added dropwise. The cooling is maintained for 4 h and then the reaction mixture is stirred at ambient temperature for 24 h. After filtration of the precipitated dicyclohexylurea, the solution is washed with $NaHCO_3$ and dried over $MgSO_4$. After evaporation of the solvent, the crude product is purified by flash-chromatography (eluent: petrol ether/ethyl acetate 20:1)

Yield: 7.40 g of colourless solid (66%), m. p.: 42°C

elemental analysis: ($C_{32}H_{53}NO_4Br_2$, M = 675.6)

calc.: 56.90% C 7.90% H 2.07% N 23.65% Br found : 57.08% C 8.09% H 2.09% N 22.06% Br



^{1}H-NMR (200 MHz, $CDCl_3$):

δ [ppm] :	7.23 (t)	[2H, H_{arom}, 3-position, b]
	6.75 (m)	[3H, H_{arom}, superposed, a+c]
	4.23 (t)	[4H, $C\underline{H}_2OOC$, e]
	3.60 (t)	[4H, $NC\underline{H}_2CH_2$, d]
	3.40 (t)	[4H, $CH_2C\underline{H}_2Br$, k]
	2.28 (t)	[4H, $OOCC\underline{H}_2CH_2$, f]
	1.85 (m)	[4H, $CH_2C\underline{H}_2CH_2Br$, i]
	1.55 (m)	[4H, $OOCCH_2C\underline{H}_2CH_2$, g]
	1.35 (m)	[24H, H_{alkyl}, h]

^{13}C-NMR (200 MHz, $CDCl_3$):

δ [ppm] :	174.1	[$OO\underline{C}CH_2$]
	147.6	[NC_{arom}]
	129.7	[C_{arom}, 3-position]
	117.3	[C_{arom}, 4-position]
	112.4	[C_{arom}, o-position]
	61.53	[$CH_2\underline{C}H_2OOC$]
	49.94	[$N\underline{C}H_2CH_2$]
	34.45	[$CH_2\underline{C}H_2Br$]
	33.10	[$OOC\underline{C}H_2CH_2$]
	29.00	[C_{alkyl}]
	28.43	[$CH_2\underline{C}H_2CH_2Br$]
	25.11	[$OOCCH_2\underline{C}H_2CH_2$]

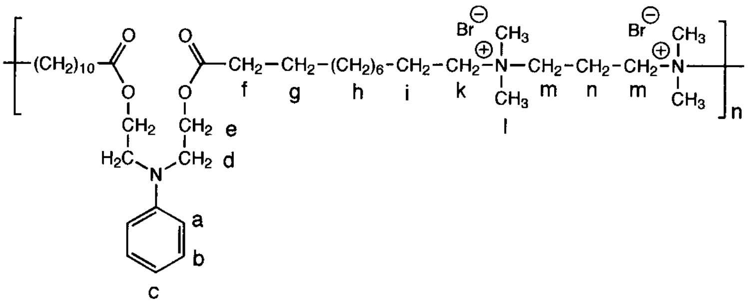
Synthesis of Polycation 1

3.26 g (4.83 mmol) of N,N-bis-[2-(11-bromoundecanoyl)-oxyethyl]-aniline (1) and 0.63 g (4.83 mmol) of N,N,N',N'-tetramethyl-1,3-propanediamine are dissolved in 12 ml of dry DMF under argon and then stirred at ambient temperature for 3 weeks. The formed polymer is precipitated in acetone, redissolved in methanol and reprecipitated in ethyl acetate. After freeze drying from water, a colourless, hygroscopic solid is obtained.

Yield: 2.65 g (68%)

elemental analysis:

calc. :	58.13% C	8.88% H	5.21% N	19.83% Br
found :	56.11% C	7,08% H	5.00% N	20.48% Br



^{1}H-NMR (200 MHz, DMSO-d_6):

δ [ppm] :		
	7.15	[2H, H_{arom}, 3-position, b]
	6.75	[2H, H_{arom}, 2-position, c]
	6.60	[1H, H_{arom}, 4-position, a]
	4.15	[4H, $C\underline{H}_2OOC$, e]
	3.57	[4H, $Ar\text{-}NC\underline{H}_2CH_2$, d]
	3.1-3.5	[4H, $CH_2\text{-}N^+C\underline{H}_2CH_2CH_2N^+\text{-}CH_2\text{-}$, k+m]
	3.10	[12H, $N^+C\underline{H}_3$, l]
	2.1-2.4	[6H, $OOCC\underline{H}_2CH_2$, $N^+CH_2C\underline{H}_2CH_2N^+$, f+n]
	1.65	[4H, $C_{alkyl}C\underline{H}_2CH_2N^+$, i]
	1.45	[4H, $OOCCH_2C\underline{H}_2C_{alkyl}$, g]
	1.20	[24H, C_{alkyl}, h]

Because in ^{1}H-NMR no end groups can be detected, the average degree of polymerization will exceed at least 20.

IR (KBr, [cm^{-1}])

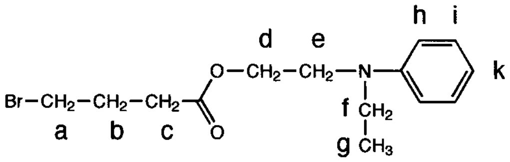
2928, 2859 (v, C-H); 1730 (v, C=O, ester); 1603 and 1500 (aromatic ring vibrations)

Synthesis of N-ethyl, N-[2-(4-bromobutanoyl)-oxyethyl-]aniline

In analogy to Neises and Steglich (Ref. 11), 1.00 g of 4-bromobutyric acid (5.99 mmol), 0.99 g 2-(N-ethylanilino)ethanol (5.99 mmol) and 37 mg of 4-dimethylaminopyridine are reacted in 30 ml of dry dichloromethane at 0°C with 1.23 g (5.99 mmol) of dicyclohexylcarbodiimide.

The mixture is allowed to stirr at 0°C for 4 h, then for another 12 h at ambient temperature. The dicyclohexylurea which precipitates is separated by filtration, then the solvent is evaporated. The crude product is purified by flash chromatography (eluent: petrol ether/ethyl acetate 5:1).

Yield: 1.46 g (77.9%) of colourless oil



^{1}H-NMR (200 MHz, $CDCl_3$):

δ [ppm] :	7.15 (m)	[2H, i]
	6.7 - 6.4	[3H, h + k superposed]
	4.10 (t)	[2H, d]
	3.5 - 3.1	[6H, a, e, f superposed]
	2.35 (t)	[2H, c]
	2.20 (m)	[2H, b]
	1.05 (t)	[3H, g]

IR (film, [cm^{-1}])
2971, 2950, 2880, (v, C-H); 1736 (v, C=O, ester); 1603 and 1500 (aromatic ring vibrations)

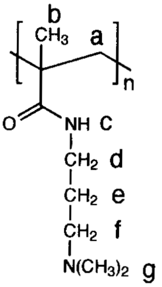
Synthesis of Poly{[N, N-[(3-dimethylamino)propyl]methacrylamide}

3.49 g (20.5 mmol) of N, N-[(3-dimethylamino)propyl]methacrylamide are dissolved in 15 ml of ethanol and 67 mg (0.38 mmol) of azobisisobutyronitrile are added. Then the degased solution is reacted at 60°C for 48 h. The polymer is precipitated in petrol ether and dried at 60°C in vacuum.

Yield: 1.27 g (36%) of colourless polymer

elemental analysis:

calc. :	63.5% C	10.7% H	16.4% N
found :	60.5% C	10.9% H	15.6% N



^1H-NMR (200 MHz, $CDCl_3$):

δ [ppm] :	7.7 - 7.4	[1H, c]
	3.3 - 3.05	[2H, d]
	2.45 - 2.3	[2H, f]
	2.2	[6H, g]
	1.75 - 1.5	[2H, e]
	1.2 - 0.75	[a + b, superposed]

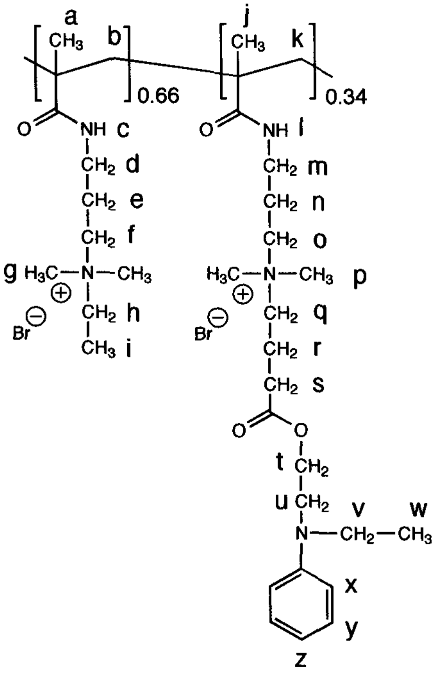
IR (KBr, [cm^{-1}])

3380 (ν, N-H); 2950, 2850, 2810, 2780 (ν, C-H); 1660 (ν, amid I); 1523 (ν, amid II); 1466 (δ, C-H);

Synthesis of Polycation 2

800 mg of poly{[N, N-[(3-dimethylamino)propyl]methacrylamide} (4.70 mmol repeat unit) and 738 mg of N-ethyl, N-[2-(4-bromobutanoyl)-oxyethyl]-aniline (2.35 mmol) are dissolved in 10 ml of dry N, N-dimethylformamide and stirred in an inert atmosphere at 60°C for four days. Then the solution is allowed to cool and an excess of bromoethane is added, the mixture is reacted at 40°C for another three days. The polymer is precipitated in ethyl acetate and then freeze-dried.

Yield: 1.75 g (97.5%)



^{1}H-NMR (200 MHz, DMSO-d_6):

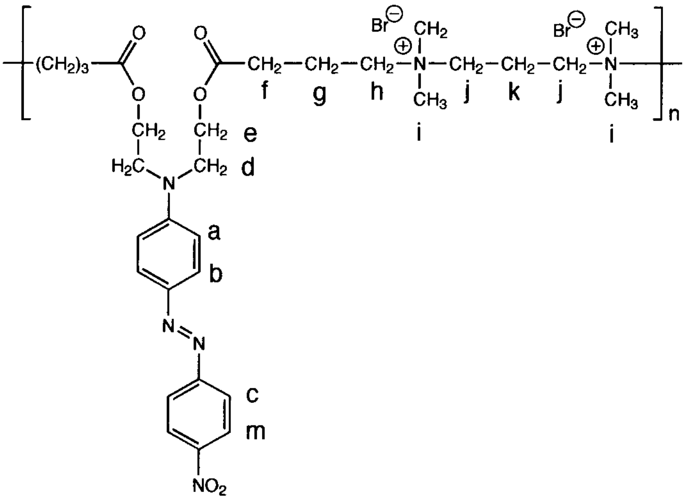
δ [ppm] :	8.5 - 7.9	[c, l, superposed]
	7.15	[y]
	6.9 - 6.5	[x, z, superposed]
	4.22	[t]
	3.9 - 2.7	[d, f, g, h, p, q, o, m, superposed and partially covered by H_2O]
	2.7 - 1.7	[b, s, u, v, r, k, superposed]
	1.7 - 0.8	[a, e, i, w, j, n, superposed]

The composition of this copolymer was determined by UV/VIS spectroscopy.

Synthesis of Polycation 4

Polycation 4 was synthesized from 4-{N, N-di-[2-(4-bromobutanoyl)-oxyethyl-]}4'-nitro-azobenzene and N,N,N',N'-tetramethyl-1,3-propanediamine in analogy to the experimental procedure for polymer 1. The synthesis of 4-{N, N-di-[2-(4-bromobutanoyl)-oxyethyl-]}4'-nitro-azobenzene is described in ref. 10.

Yield: 89% of red solid



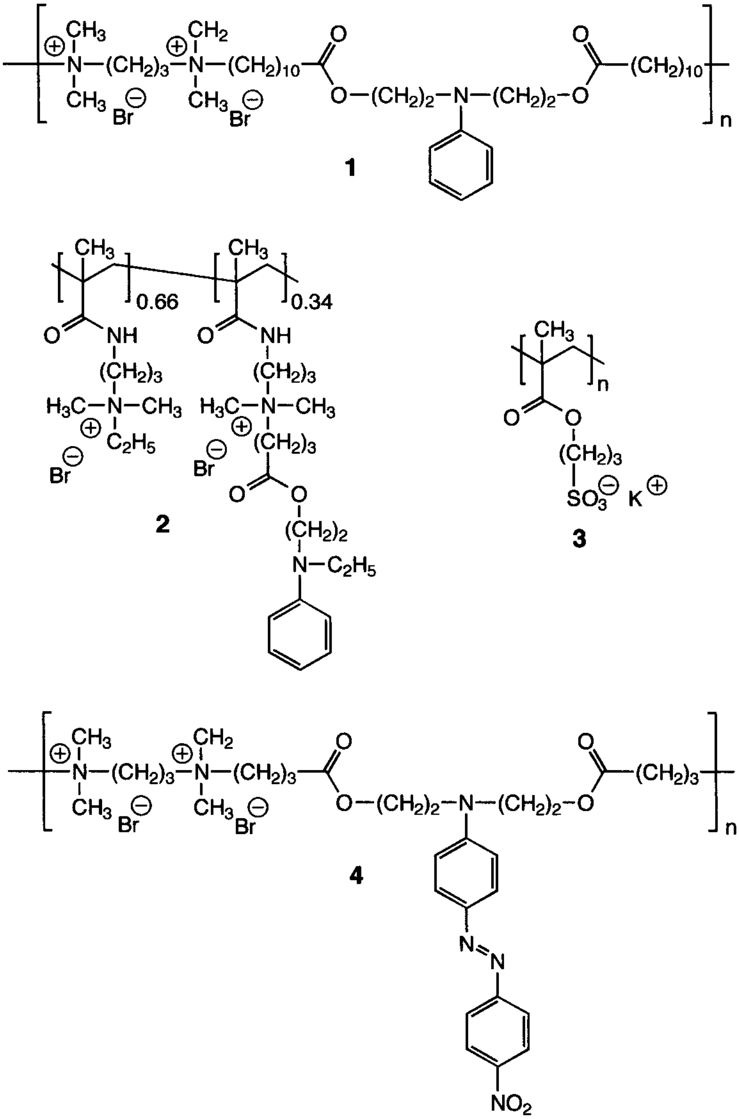
^{1}H-NMR (200 MHz, D_2O):

δ [ppm] :	7.5	[m]
	7.3 - 7.0	[b + c, superposed]
	6.45	[a]
	4.15	[e]
	3.9 - 2.8	[d, h, i, j, superposed]
	2.7 - 1.7	[f, g, k, superposed]

In ^{1}H-NMR, no end groups can be detected, therefore the average degree of polymerization will exceed at least 20.

IR (KBr, [cm^{-1}])
2967, 2880 (ν, C-H); 1731 (ν, C=O, ester); 1601 and 1516 (aromatic ring vibrations), 1340 (ν_{sym}, NO_2)

Fig. 1 Chemical structures of the polymers employed in this work



Alternating Polyelectrolyte Deposition

In a first set of experiments, the build-up of multilayers (see figure 2) was performed by alternating deposition of the polycations and poly(sulfopropyl)methacrylate **3** without a reaction at the surface to verify the suitability of the polycations **1** and **2** for polyelectrolyte multilayer assembly. Pretreated quartz substrates (Ref. 4) were used for all experiments. For each deposition step, the immersion time in the polymer solution was 20 minutes.

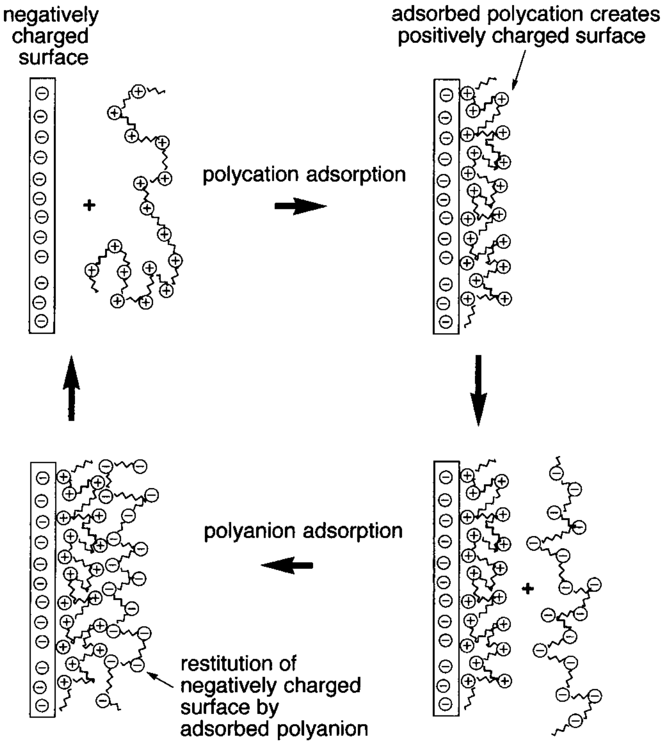


Fig. 2 Schematic representation of multilayer assembly by alternating polyelectrolyte deposition

The progression of the assembly was monitored by the UV spectroscopy. In figure 3, the depencences of the absorbances on the number of deposition cycles are shown for the pairs 1/3 and 2/3.

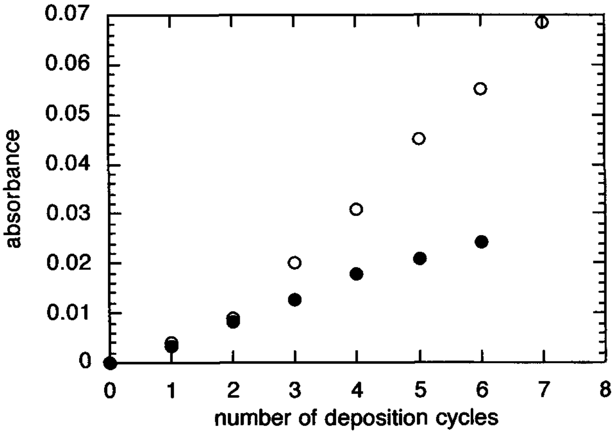


Fig. 3 Dependence of the absorbance at 260 nm on the number of deposition cycles for the multilayer systems **1**/**3** (•) and **2**/**3** (o)

The increase of the absorbance with every step is a proof for the successful deposition of material in every cycle. For the assembly prepared from the ionene-type polycation **1** and **3**, we obtain a linear increase of the absorbance with the number of deposition cycles. In contrast to this, the absorbance increases in a nonlinear way for multilayers prepared from the side-chain polycation **2** and **3** for the first layers. The nonlinear growth of an assembly is frequently encountered for polyions with hydrophobic substituents (Refs. 6 and 10), but still, the behaviour depends on the detailed chemical structure in a non-trivial way: ionene **1** incorporates long alkyl chains, too, but its deposition does not give rise to a nonlinear increase of the absorbance.

Modified Deposition with Reaction Step

In the modified deposition process, a reactive modification step is introduced between the polycation and the polyanion deposition (figure 4). The aniline residues of the polycations are coupled with the diazonium salt of 4-nitroaniline at the surface.

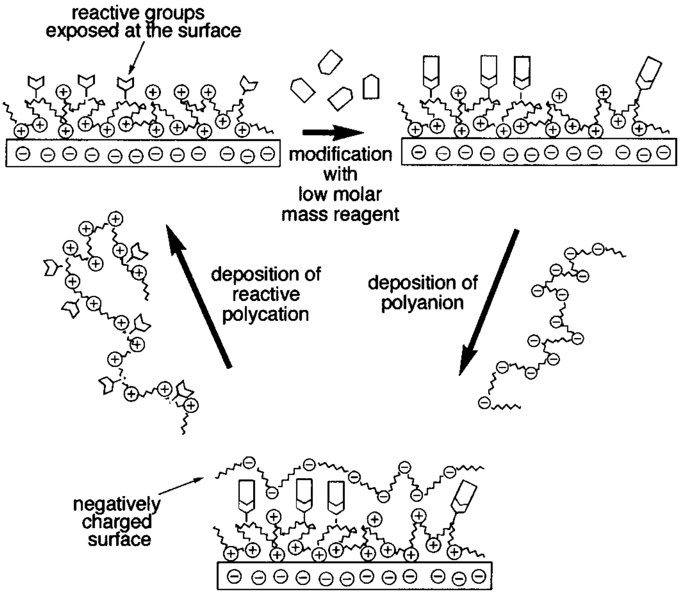


Fig. 4 Schematic representation of modified multilayer deposition with reaction step at the surface

As first example, the deposition with polycation 1 is discussed. Both polycations and polyanions were allowed to adsorb for 20 minutes at ambient temperature, the time for azo coupling at the surface was 30 minutes at 0°C. After a few deposition steps, the samples appear red to the bare eye, on a macroscopic scale, no defects can be detected in the modified coating. The polycation deposition and the reactive modification were monitored by UV/VIS spectroscopy. Spectra were taken after every adsorption step of the polycation and after every azo coupling step. The dependence of the absorbances at 260 nm and at 450 nm on the number of adsorption cycles are shown in figure 5.

Although the surface is modified with uncharged groups, the deposition is successful, as demonstrated by the increase of the absorbance at 260 nm. However, different from the use of the unmodified polycation 1, the increase of the absorbance is no longer linear. This may be due to the addition of bulky uncharged groups at the surface by the coupling reaction. The increase of the absorbance becomes similar to the behaviour often encountered for polymers carrying hydrophobic groups (Ref. 10). Nevertheless, the assemblies obtained exhibit a uniform colour and a homogeneous appearance.

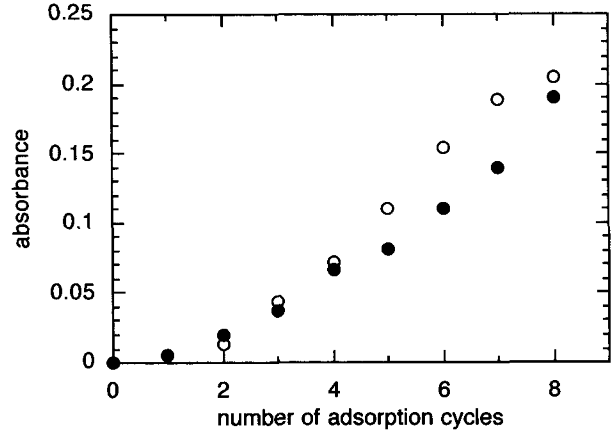


Fig. 5 Dependence of the absorbance at 260 nm before coupling step (o) and at 450 nm after coupling step (•) on the number of adsorption cycles for multilayers of **1**/**3** modified by azo coupling at the surface

After every reactive modification, the absorbance at 450 nm increases, indicating the formation of azo moieties and therefore the success of the interfacial reaction. As for the absorbance at 260 nm, the increase shows a nonlinear behaviour. This is not surprising, with the amount of polycation deposited slightly increasing in every step, an increase in the number of moieties reacting at the surface is expected.

The same conditions as for reactive polycation **1** were chosen for a first experiment of the multilayer deposition with interfacial reaction for polycation **2**. Again, a nonlinear increase in the absorbance in the UV and in the visible range is encountered (figure 6).

In an additional experiment with polycation **2**, the time for the interfacial azo coupling reaction was extended to 60 minutes, while the adsorption times for the polyions were kept constant (figure 7).

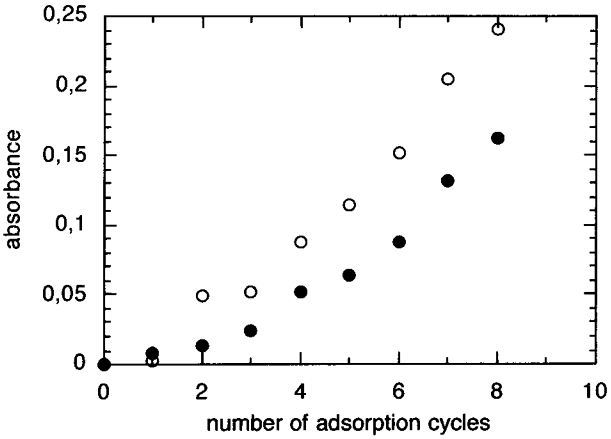


Fig. 6 Dependence of the absorbance at 260 nm before coupling step (o) and at 470 nm after coupling step (•) on the number of adsorption cycles for multilayers of 2/3 modified by azo coupling at the surface, reaction time 30 min at 0°C.

At a first glance, the results are similar to the data for 30 minutes of reaction time, but the signal level is generally higher. This may be explained by a higher degree of conversion, since the azo chromophores formed in the surface reaction not only give rise to the absorbance in the visible range, but also contribute to the absorbance in the UV range. In contrast to the experiment with 30 minutes of reaction time, the samples become turbid to a signifcant extent after several deposition cycles. Possibly, with longer reaction time, the diffusion of the low molar mass reagent into the assembly becomes more important and causes a higher disorder in the multilayer arrangement, reducing the optical quality of the assembly.

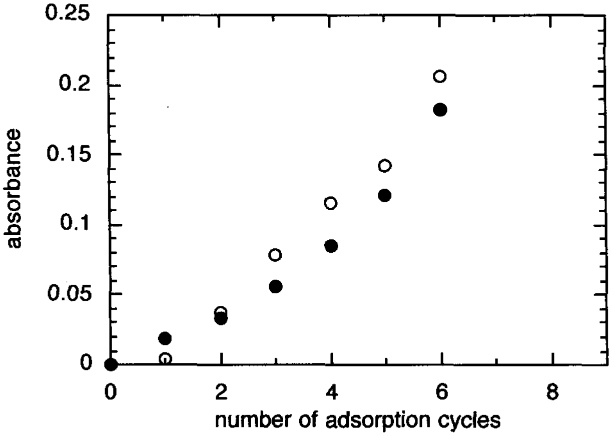


Fig 7 Dependence of the absorbance at 260 nm before coupling step (o) and at 470 nm after coupling step (•) on the number of adsorption cycles for multilayers of **2**/**3** modified by azo coupling at the surface, reaction time 60 min at 0°C.

Differences between Multilayer Assemblies with Different Polycations

Although the qualitative features of chemically modified assemblies made from **1**/**3** and **2**/**3** are rather similar, some quantitative differences are observed. Whereas the absorbances at 260 nm of multilayers of **1**/**3** and of **2**/**3** are nearly the same, the values of the absorbance in the visible range after the coupling reaction are smaller for assemblies with polycation **2** when equal reaction times are compared. This may reflect different accessibilities of the aniline moiety in the multilayers, or alternatively, different diffusion rates of the reagent. In any case, it becomes clear that the positioning of the reactive groups within the polyelectrolyte will influence its chemical reactivity.

Even more prominent, there is a significant difference in the λ_{max} values of the visible absorbance for the two polycations. Compared to the spectrum of model polymer **4** in solution (λ_{max} = 460 nm), the value for polycation **1** is blue-shifted to 450 nm for the chromophore which is formed in the surface reaction. This finding is in agreement with the results of a previous study, where polymer **1** was employed for a different kind of multilayer build-up process which also includes an azo coupling at the surface (Ref. 12). For polymer **2** however, a red shift is visible compared to the two other spectra with an absorbance maximum at

470 nm. These differences in λ_{max} probably reflect the response of the chromophores to the different environments provided by the different polymeric fragments of the ionene-type polycation 1 and the side chain polycation 2. It should be emphazied that the azo chromophore employed in this study is highly solvatochromic and seems to be influenced by its polymeric environment even in solution. Also , aggregation phenomena may play a role.

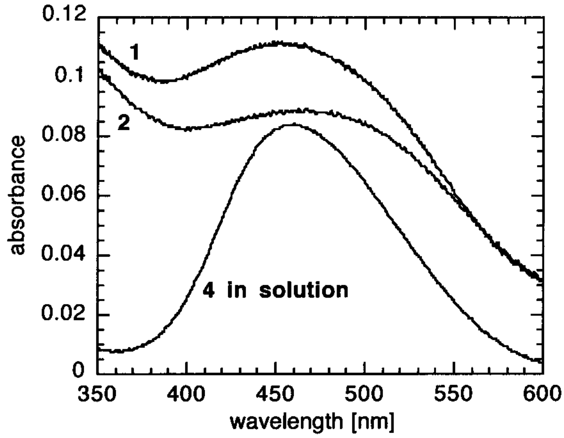


Fig. 8 (a) spectrum of an assembly incorporating polymer **1** azo coupled at the surface
(b) spectrum of an assembly incorporating polymer **2** azo coupled at the surface
(c) spectrum of model polymer **4** in aqueous solution

CONCLUSION AND PERSPECTIVES

By incorporating aniline moieties into polycations, it is possible to obtain polyelectrolyte multilayers which can be modified by an azo coupling reaction. Different from previous studies of such a reactive modification, this reaction requires the attack of a low molar mass reagent at the surface. Although a reaction within the assemblies may be sterically rather demanding, the multilayer deposition and the modification are successful and uniform coatings are obtained. Polycations bearing the reactive group at different positions in the polymer, i.e. close to the backbone and in the side chain gave rise to different behaviour, underlining once more the importance of the detailed structure of the polyelectrolytes used. For example, the efficiencies in the coupling reaction as well as the positions of the absorbance maxima λ_{max}

differ though the newly formed chromophore is identical. The difference in λ_{max} presumably reflects the influence of the different environments on the chromophore.
Due to the reaction in a confined space at the interface, an - at least partially - oriented arrangement of the chromophores formed at the interface is possible. Since the azo chromophore used in this study is known for a high second order nonlinear optical (NLO) coefficient, it should be possible to study an orientation by NLO techniques. One may even speculate whether by such a modification polyelectrolyte multilayers can be obtained which exhibit a pronounced nonlinear optical activity.

ACKNOWLEDGEMENT

Technical assistance by M. El Guweri is gratefully acknowledged. Financial support for the work was provided by the DG Recherche Scientifique of the French Community of Belgium (convention 94/99-173).

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