Polyelectrolyte Multilayer Assemblies Containing Nonlinear Optical Dyes

André Laschewsky* and Erik Wischerhoff

Department of Chemistry, Université Catholique de Louvain, Place Louis Pasteur 1, B-1348 Louvain-la-Neuve, Belgium

Martti Kauranen and André Persoons

Laboratory of Chemical and Biological Dynamics and Center for Research on Molecular Electronics and Photonics, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Heverlee, Belgium

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ABSTRACT: An ionene-type polycation incorporating a nonlinear optical chromophore was synthesized. It was employed for the assembly of alternating polyelectrolyte multilayers on charged and uncharged substrates, using different organic polyanions as well as montmorillonite clay as anionic counterparts. The assembly process was followed by UV/vis spectroscopy. The influences of the choice of anionic species and of variations in the layer architecture were studied. Different kinds of aggregation were observed for different species of polyanions employed, and the increase of absorbance with the number of layers proved to be dependent on the specific multilayer composition. The degree of orientation of the chromophores was investigated by second-harmonic generation and the nonlinear response was found to depend strongly on the anionic species. This result demonstrates that polyelectrolyte multilayers do not necessarily have a centrosymmetric structure, as generally assumed.

Introduction

By alternation of adsorption of oppositely charged polyelectrolytes, multilayer assemblies can be obtained on charged surfaces.[1−3] While many studies focus on simple commercial polyelectrolytes like poly(allylamine), poly(vinyl sulfate), and poly(styrenesulfonate)[4−6] as polymeric components for the assembly, there are also examples for the employment of charged polyions containing dye moieties,[7−10] which offer some analytical advantages: First of all, colored systems allow for the rapid and nondestructive evaluation of the macroscopic quality and of the homogeneity of the thin films by the bare eye and by optical microscope, complementing the various high resolution analytical methods for thin coatings which focus on microscopic spots. In addition, the dye may serve as an internal probe in the assembly, revealing, e.g., solvatochromic or metachromic effects caused by the polyionic counterpart, birefringence, or aggregation phenomena.

Up to now, little attention has been paid to the alignment (parallel/antiparallel arrangement of the long axes of molecules or moieties) or even to the orientation (parallel arrangement of long axes and of substituents) of polymer fixed dye moieties in polyelectrolyte multilayers. Though first hints may be derived from the UV/vis spectra, the effects in the electronic spectra are often small and therefore not easy to interpret. Therefore, in order to be able to gain further information, we synthesized a polycation which incorporates the well-known second-order nonlinear optical (NLO) dye 4-(*N*,*N*-dialkylamino)-4′-nitroazobenzene and employed it for polyelectrolyte multilayer assembly. In this way, not only could we obtain information about the behavior of the dye polycation in multilayers of different composition by visible spectroscopy, but also the NLO response enabled us to derive additional information about the orientation of the chromophores from second-harmonic generation experiments.

Experimental Section

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. For infrared measurements, a 1710 infrared Fourier transform spectrometer from Perkin-Elmer was used. The second harmonic generation measurements were performed with the fundamental (1064 nm) output of a Q-switched Nd:YAG laser (Spectra Physics Quanta-Ray GCR-130-50, ~10 ns pulse length, 50 Hz repetition rate). The beam of the Nd:YAG laser (1064 nm) was weakly focused to a spot size of 1−2 mm on the sample. The angle of incidence was 45°, and second-harmonic radiation at 532 nm was detected in the reflected direction. The incident pulse energies were in the range 1−10 mJ. To avoid interference between second-harmonic radiation generated from the front and back surfaces of the samples, the multilayers were deposited on 6 mm thick glass substrates. Only the signal from the film deposited on the front surface was detected. The second-harmonic light was separated from the fundamental beam by an infrared-blocking filter and a 532 nm interference filter before detection by a photomultiplier and signal processing electronics.

Materials. The water for all experiments was deionized and purified by an Elgastat Maxima from Elga (resistance 18.2 MΩ). 4-Bromobutyric acid, *N*-phenyldiethanolamine, dicyclohexylcarbodiimide, 4-(dimethylamino)pyridine, branched poly(ethyleneimine) (**PEI**), poly(vinyl sulfate) (**PVS**), and poly(styrenesulfonate) (**PSS**) were purchased from Aldrich and used without further purification. 3-Sulfopropylmethacrylate (**SPM**) and bis-(3-sulfopropyl)itaconate (**SPI**) were gifts from the Raschig GmbH, Germany. **SPM** was used as delivered; **SPI** was recrystallized twice from methanol prior to polymerization. An aqueous suspension of deliminated montmorillonite clay ($Al[Si_2O_5](OH)$) containing Na, K, Mg, and Ca ions) was kindly provided by Dr. Nicolas A. Khotov.[11] This dispersion was diluted to one-fifth with water and centrifuged at 3000 rpm for 20 min prior to use in the assembly process to remove undeliminated particels.

Synthesis of the Polymers. **SPM** and **SPI** were polymerized in aqueous solution with a monomer concentration of approximately 0.3 mol·L^{-1} at 70 °C with 1 mol % of potassium peroxodisulfate as initiator. Then 48 h of polymerization time gave a quantitative yield. The synthetic route to the NLO dye polycation is as follows: the first step is the esterification of *N*-phenyldiethanolamine with 4-bromobutyric acid with dicy-

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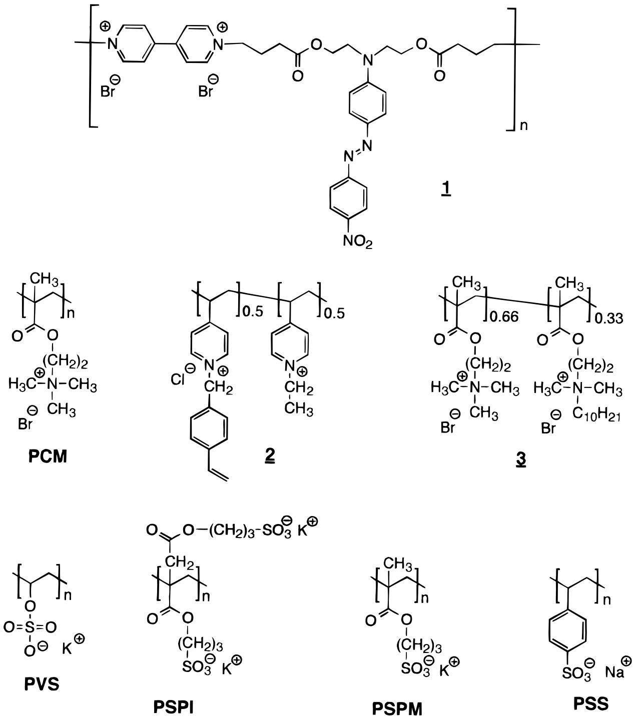
Chart 1. Polymers Used in This Study



clohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in dichloromethane, in analogy to ref 12. Then the obtained ester is coupled with the diazonium salt of 4-nitroaniline to give an azo dye by standard procedures.[13] This azo dye is then reacted with 4,4′-dipyridyl in *N*,*N*-dimethylformamide to give the ionene-type polycation **1**.

The formulae of all polymers used for this study are depicted in Chart 1. Polymer **2** was obtained by stepwise quaternization of poly(4-vinylpyridine), first with 4-vinylbenzyl chloride and then with bromoethane. Details of the experimental procedure will be published elsewhere.[14] The synthesis of polymer **3** was already described;[15] **PCM** is synthesized in an analogous manner.

Preparation of the Polyelectrolyte Multilayers. The polyions were dissolved in water with a concentration of 0.02 mol of repeat unit per liter, except for polymer **1**, where a saturated aqueous solution—lower in concentration—was used. As substrates for the multilayer assemblies, float glass plates were used, which were cleaned and pretreated as described in ref 15. In the cases where polypropylene foils served as substrate, the polypropylene was thoroughly washed with distilled ethanol and then rinsed with ultrapure water. One initial buffer layer of PEI (glass substrates) or polymer **3** (polypropylene) was deposited onto all substrates, prior to subsequent deposition of the various polyelectrolytes. Multilayers were assembled by alternating dipping of the substrates into the solution of the polyions for 20 min each. Before changing the polyelectrolyte solutions, the substrates were dipped into three beakers with pure water subsequently for 1 min each, to remove adhering excess solution. The photocrosslinking of polycation **2** was done by irradiating with a UV lamp at 254 nm for 1 min after each deposition step of this polymer.

***N*,*N*-Bis[2-((4-bromobutanoyl)oxy)ethyl]aniline (1).** A solution of 2.50 g of *N*-phenyldiethanolamine (13.8 mmol), 4.80 g of 4-bromobutyric acid (28.7 mmol) and 50 mg of 4-(dimethylamino)pyridine in 20 mL of dry dichloromethane are cooled to 0 °C. Then 5.92 g (28.7 mmol) of dicyclohexylcarbodiimide are added in 10 mL of CH_2Cl_2. The mixture is allowed to stirr at 0 °C for 4 h, then at ambient temperature for another 12 h. The precipitated dicyclohexylurea is filtered off and the solvent is removed. Then the crude product is purified by flash chromatography (eluent: petrol ether/ethyl acetate 3:2).

Yield: 3.97 g (60%) of colorless oil.

^1H-NMR (200 MHz, $CDCl_3$): 7.23 (m, 2H, $H_{arom,\ m-pos}$), 6.75 (m, 2H, H_{arom}, *o*- and *p*-pos), 4.26 (t, 4H, CH_2OOC), 3.63 (t, 4H, NCH_2CH_2), 3.44 (t, 4H, CH_2CH_2Br), 2.49 (t, 4H, $OOCCH_2CH_2$), 2.14 (m, 4H, $CH_2CH_2CH_2Br$).

^{13}C-NMR (200 MHz, $CDCl_3$): 172.4 ($OOCCH_2$), 147.3 (NC_{arom}), 129.5 (C_{arom}, *m*-pos), 117.1 (C_{arom}, *p*-pos), 112.1 (C_{arom}, *o*-pos), 61.5 (CH_2CH_2OOC), 49.6 (NCH_2CH_2), 32.7 (CH_2CH_2Br), 32.3 ($OOCCH_2CH_2$), 27.6 ($CH_2CH_2CH_2Br$).

IR (film): 3035 and 3010 cm^{-1} (=C−H_{arom} valence), 2956 and 2925 cm^{-1} (C−H_{alkyl} valence), 1735 cm^{-1} (C=O valence), 1601 and 1504 cm^{-1} (aromatic ring vibration).

4-{*N*,*N*-Bis[2-((4-bromobutanoyl)oxy)ethyl]}4′-nitroazobenzene (2). To prepare the diazonium salt for the azo coupling, 0.29 g (2.20 mmol) of 4-nitroaniline are dissolved in 3 mL of semiconcentrated hydrochloric acid and cooled to 0 °C. A cooled (0 °C) solution of 0.145 g (2.10 mmol) of sodium nitrite in 1.5 ml of water is added dropwise with rapid stirring. After 15 min at 0 °C, a small amount of urea is added to this solution to destroy residual nitrite. Then 1.00 g (2.09 mmol) of monomer **1** are dissolved in 7 mL of 2-propanol and 1 mL of acetone and cooled to 0 °C. The diazonium salt solution is added dropwise while stirring. After the addition is completed, the mixture is stirred for another 4h at 0 °C. The solvent is removed and the crude product is purified by flash chromatography (eluent: petrol ether/ethyl acetate 3:1).

Yield: 0.88 g (67%) of red crystals.

^1H-NMR (200 MHz, $CDCl_3$): 8.3 (d, 2H, H_{arom}, ortho to NO_2), 7.9 (2d, 4H, H_{arom}, superposed signals of H ortho to azo group), 6.8 (d, 2H, H_{arom}, ortho to amino group), 4.3 (t, 4H, CH_2CH_2OOC), 3.8 (t, 4H, $BrCH_2CH_2$), 3.5 (t, 4H, NCH_2CH_2O), 2.5 (t, 4H, $BrCH_2CH_2CH_2$-COO), 2.1 (m, 4H, $BrCH_2CH_2CH_2COO$).

^{13}C-NMR (200 MHz, $CDCl_3$): 172.4 ($OOCCH_2$), 156.2 ($N{=}NC_{arom}$), 155.5 (NC_{arom}), 147.8 (O_2NC_{arom}), 144.3 ($N = NC_{arom}$), 124.0 (C_{arom}, *o*-pos to NO_2), 122.1 (C_{arom}, *o*-pos to N = N), 111.9 (C_{arom}, *o*-pos to amino group), 61.5 (CH_2CH_2OOC), 49.6 (NCH_2CH_2O), 32.7 (CH_2CH_2Br), 32.3 ($OOCCH_2CH_2$), 27.6 ($CH_2CH_2CH_2Br$).

IR (KBr): 3078 and 3004 cm^{-1} (=C−H_{arom} valence), 2961 and 2925 cm^{-1} (C−H_{alkyl} valence), 1738 cm^{-1} (C=O valence), 1602 and 1518 cm^{-1} (aromatic ring vibration).

Polymer 1. A solution of 0.880 g (1.40 mmol) of azo dye (monomer **2**) and 0.219 g (1.40 mmol) of 4,4′-dipyridyl in 3 mL of dry DMF is heated to 60 °C for 72 h. The polymer is precipitated in ethyl acetate and freeze dried. Then it is redissolved in DMSO, reprecipitated in ethyl acetate, and again freeze dried.

Yield: 0.93 g (84.6%).

^1H-NMR (200 MHz, DMSO-d_6): 9.4 (d, 4H, H_{arom}, ortho to N of quaternized dipyridyl group), 9.3 (d, H_{arom}, ortho to N of quaternized dipyridyl end group), 8.9 (superposed, 4H, H_{arom}, meta to N of quaternized dipyridyl group and H_{arom}, meta to N of quaternized dipyridyl end group), 8.7 (d, H_{arom}, ortho to N of unquaternized dipyridyl end group), 8.4 (d, 2H, H_{arom}, ortho to NO_2), 8.1 (d, H_{arom}, meta to N of unquaternized dipyridyl end group), 7.9 (2d, 4H, H_{arom}, superposed signals of H ortho to azo group), 7.1 (d, 2H, H_{arom}, ortho to amino group), 4.8 (broad, 4H, $N^+CH_2CH_2CH_2COO$), 4.4 (broad, 4H, $COOCH_2CH_2$), 3.8 (broad, 4H, NCH_2CH_2O), 2.6 (covered by DMSO signal, $CH_2CH_2CH_2COO$), 2.3 (broad, 4H, $CH_2CH_2CH_2COO$).

^{13}C-NMR (200 MHz, DMSO-d_6): 172.5 ($OOCCH_2$), 156.2 ($N = NC_{arom}$), 155.5 (NC_{arom}), 151.7 (C ortho to quarternized N), 149.0 (C para to quarternized N), 147.8 (O_2NC_{arom}), 146.2 (C meta to quarternized N), 143.8 ($N = NC_{arom}$), 127.0 (C_{arom}, *o*-pos to NO_2), 124.3 (C_{arom}, *o*-pos to N = N), 122.4 (C_{arom}, *o*-pos to N = N), 112.1 (C_{arom}, *o*-pos to amino group), 62.0 ($CH_2CH_2N^+$), 60.5 (CH_2CH_2OOC), 49.6 (NCH_2CH_2O), 30.8 ($OOCCH_2CH_2$), 26.5 ($CH_2CH_2CH_2N^+$).

IR (KBr): 3077 and 3008 cm^{-1} (=C−H_{arom} valence), 2980 and 2960 cm^{-1} (C−H_{alkyl} valence), 1729 cm^{-1} (C=O valence), 1640 cm^{-1} (ring vibration of the quaternized heterocycle), 1602 and 1515 cm^{-1} (aromatic ring vibration).

Results and Discussion

Preparation of Polycation 1. Polycation **1** is prepared by standard procedures. The 200 MHz ^1H-NMR-spectrum of this ionene in DMSO-d_6 is shown in

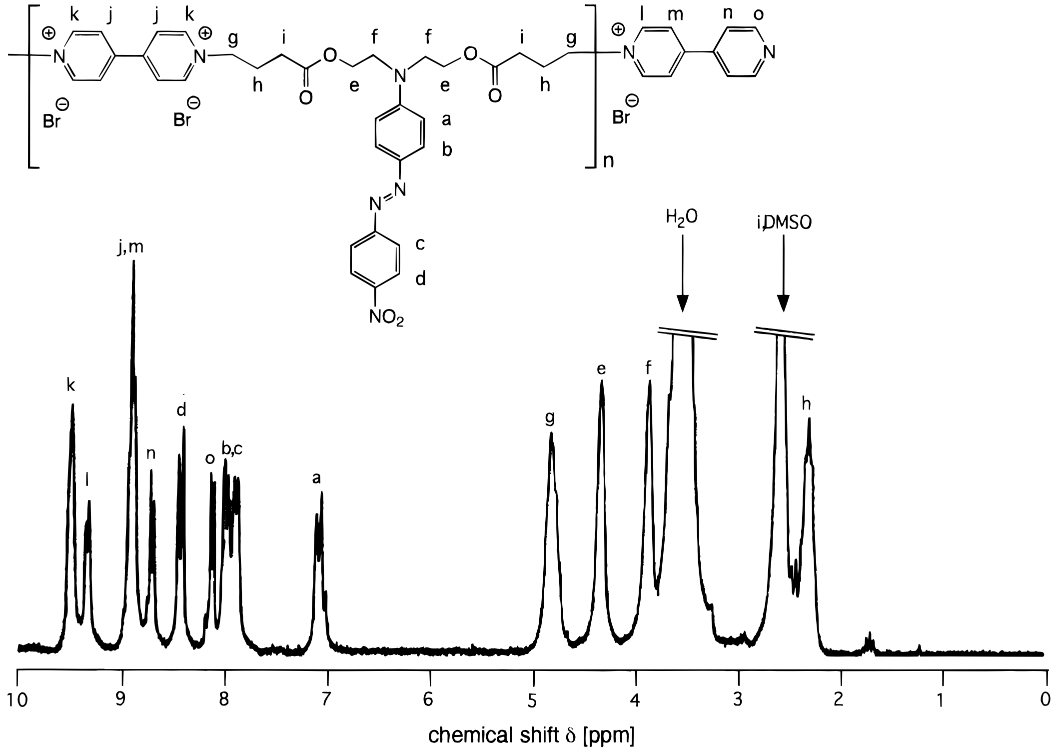


Figure 1.

Figure 1. In this spectrum, end group signals are still visible, which can be assigned to only monoquaternized 4,4′-dipyridyl groups; a rather common feature of viologen polyelectrolytes.[17] On the other hand, as can be verified by the spectrum in D_2O, no end group signals of the bromine-terminated alkyl chains are visible. This behavior reflects the influence of the first quaternization of the 4,4′-dipyridyl unit on the reactivity of the second heterocyclic ring. Electron density is withdrawn from this second heterocycle by the quaternized nitrogen in the first ring, and therefore the reactivity of the second nitrogen is lower.

As a consequence, the degree of polymerization of polymer **1** is limited. A comparison of the the integration of the viologen units and the monoquaternized 4,4′-dipyridyl groups yields an average degree of polymerization of approximately 2.5. Due to the rather high molar mass of the repeat unit, the average molar mass of the polymer is about 2000, which corresponds to six charges per chain on average.

UV/Vis Spectra of Polycation 1 in Solution. Figure 2 shows a comparison of the UV/vis spectra of polymer **1** in aqueous solution, in methanol and in ethanol. The polymer exhibits a broad, rather symmetric band in the visible range, for which a pronounced solvatochromic effect is encountered. This is not unexpected for a polymer incorporating a strong donor-acceptor dye. In aqueous solution, a maximum at 488 nm is found. The spectra in the organic solvents are more blue-shifted. In methanol, we find a maximum at 459 nm, while the λ_{max} in ethanol is at 458 nm. As the visible-spectrum of the dibromide precursor azo dye in methanol is virtually the same as for polymer **1**, no particular polymer effect seems to occur in the spectra.

Multilayer Assemblies of 1 with Different Anionic Counterparts. Multilayer buildups of **1** can be assembled with a number of different polyanions which are stable in water. In organic solvents they are stable when glass substrates are used, but partial dissolution is observed for polypropylene as substrate. The assemblies are homogeneous as regarded by eye and in the light microscope with a 100× magnification. No birefringence can be detected between crossed polarizers, which indicates the buildups are isotropic in plane. Different polyanions used to constitute the multilayer assemblies lead to significantly different UV/vis spectra (Figure 3). All spectra with organic polyanions are blue shifted compared to the spectrum in aqueous solution. The most pronounced blue shifts are seen for polyanions consisting of aliphatic structures with anionic sulfo groups. With **PVS** and **PSPI**, the species with the highest charge densities, the maximum of absorbance is 443 nm, the lowest value of this study. **PSPM**, which is somewhat lower in charge density, induces λ_{max} at 468 nm. The aromatic polyanion **PSS** exhibits a maximum at 478 nm. Noteworthy, in all cases, the spectra show a shoulder at longer wavelengths.

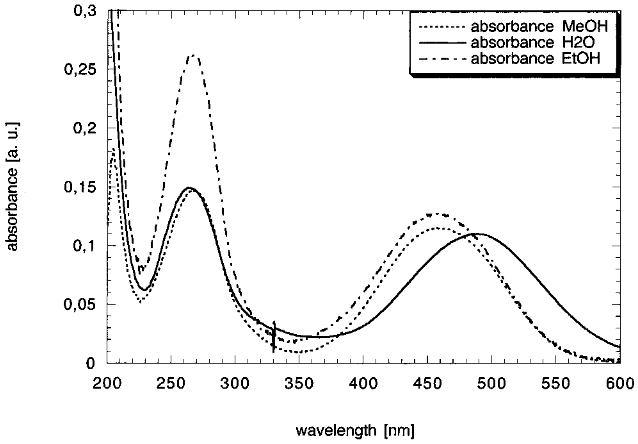


Figure 2. UV/vis spectra of polycation **1** in water, methanol, and ethanol.

In contrast to the organic polyanions, the use of montmorillonite clay as inorganic polyanion in the assembly gives rise to a red shift (λ_{max} = 500 nm)

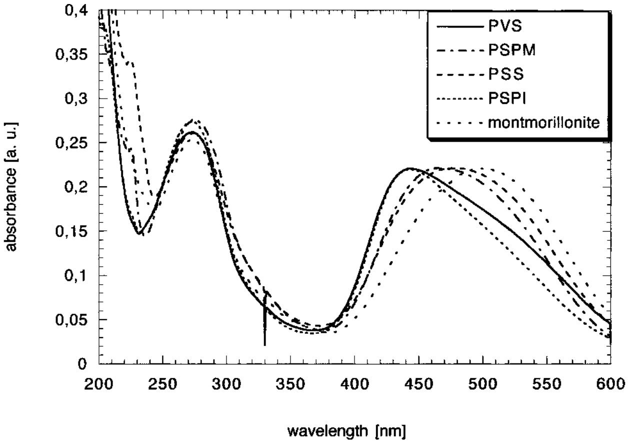


Figure 3. UV/vis spectra of multilayer assemblies of polycation **1** with different polyanions.

compared to the aqueous solution spectrum, with a shoulder around 470 nm being present.

Presumably, the different anions used in the assemblies lead to different aggregation phenomena. The blue shifts in the spectra may be explained by H-aggregates, while in the assembly with montmorillonite, J-aggregates may exist. However, the shoulders present in all spectra indicate that there is no strict ordering in the layers and still a considerable amount of nonaggregated dye moieties may be still present.

Figure 4a–d shows the dependence of the absorbance on the number of deposition cycles for different multilayer assemblies. The increase of absorbance with the number of deposition cycles is strongly dependent on the specific layer architecture. When **PVS**, **PSPI**, and **PSPM** are employed as polyion counterpart (Figure 4a), a nonlinear growth in absorbance is observed with increasing number of adsorbed layers. It has to be emphasized that this assembly behavior is not due to artifacts caused by irregularly treated substrates as proposed for some examples in the literature.[18] It is highly reproducible even on different kinds of substrates: e.g., the same growth behavior is found on glass and on polypropylene. Furthermore, it is independent of the number of buffer layers used. We have encountered this phenomenon frequently for polymers carrying high contents of hydrophobic groups[19] such as **1** whereas in contrast a nonlinear increase in absorbance does not occur for multilayer assemblies made of polyelectrolytes with a high content of hydrophilic groups.

Nevertheless, it is possible to adjust the adsorption to a linear growth by different strategies: For the polyion pair **1/PSS** the first cycle results in a weak absorbance, but then the absorbance increases linearly (Figure 4b). When delaminated montmorillonite clay is deposited as anionic component (Figure 4b), the increase in absorbance is weaker than for all other examples, but strictly linear starting with the very first layer. We also do obtain a linear growth with **PVS** as polyanion when a layer of the cross-linkable polymer **2** cross-linked immediately after the deposition is introduced into the assembly for every second polycation layer instead of **1**: the first adsorption shows a relatively weak intensity, but then the growth of absorbance is strictly linear (Figure 4d). The cross-linking seemes to be essential: when **PVS** is maintained as polyanion, but every second polycation layer is replaced by **PCM**—a polycation which usually gives rise to a linear growth behavior—the nonlinear increase in absorbance persists (Figure 4c).

It is possible that the nonlinear increases in absorbance are caused by a somewhat irregular deposition

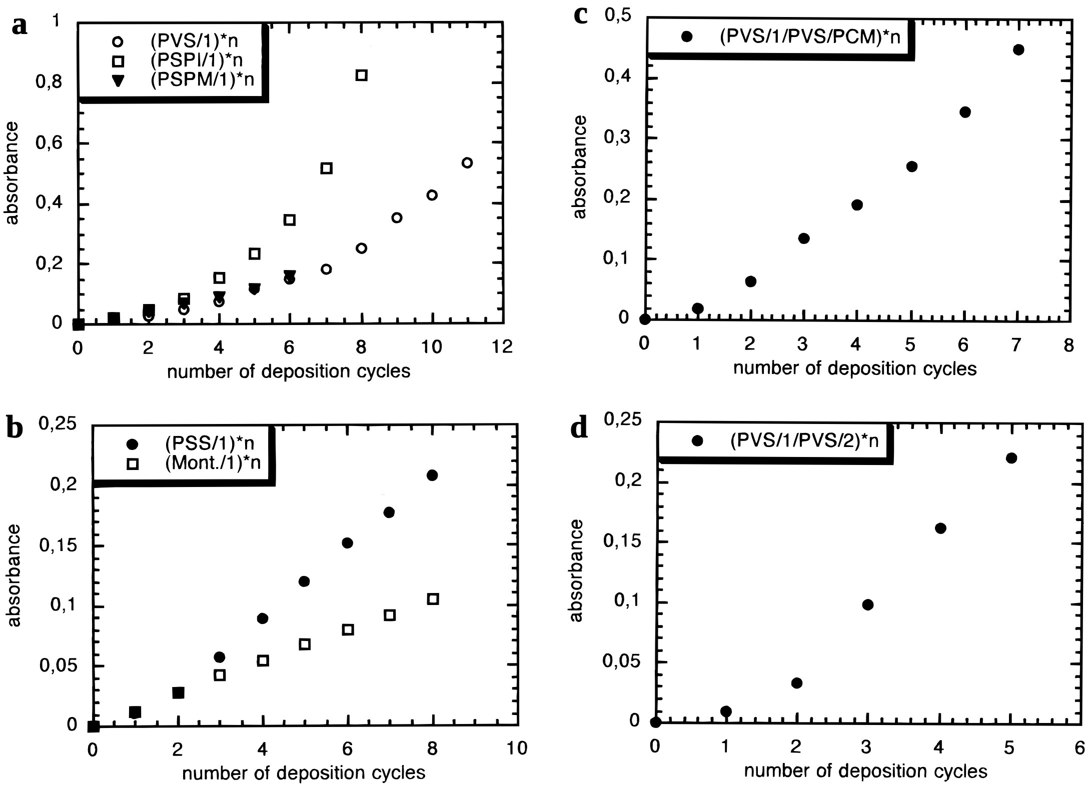


Figure 4. (a) Plot of absorbance vs number of deposition cycles for the systems **PVS/1**, **PSPI/1**, and **PSPM/1**. (b) Plot of absorbance vs number of deposition cycles for the systems **PSS/1** and montmorillonite/**1**. (c) Plot of absorbance vs number of deposition cycles for an assembly of the structure (**PVS/1/PVS/PCM**)$_n$. (d) Plot of absorbance vs number of deposition cycles for an assembly of the structure (**PVS/1/PVS/2**)$_n$.

of the polycation dye on the surface, creating a rougher surface with dangling polymer loops and tails, in which the next polyion can interpenetrate. Thus the surface is roughened even more, and more material can be deposited in the next step, resulting in a nonlinear growth of the multilayers. Given that this explanation is correct, the cross-linked layers of polycation **2** or the rigid anionic sheets of montmorillonite clay will block the interpenetration. Hence, disorder and roughness on the surface do not increase, which leads to the linear growth in absorbance, as observed.

The linear increase in absorbance in the case of **1**/**PSS** is more difficult to explain. Perhaps not only the electrostatic forces but also $\pi-\pi$ interactions of the aromatic rings in **PSS** and **1** play a role in the deposition process of this system. Additional interactions between the polymers might give rise to a more flat and regular deposition of **1**, thus suppressing the interpenetration and increase in surface roughness. As **PSS** is the most hydrophobic of the organic polyanions used and the tendency to nonlinear growth increases with the charge density, an alternative explanation may be considered. Perhaps a better match of the distances between charged groups in polycation and polyanion leads to a flatter deposition with less loops, thus preventing an increase in the amount of polymer deposited in the following steps.

It is noteworthy that the blue shifts in the VIS spectra of the multilayer assemblies and the charge density of the organic polyanions coincide: The higher the charge density in the polyanion, the more pronounced is the blue shift.

Multilayer Assembly on Uncharged Substrates. Typically, polyelectrolytes are thought to bind directly to a charged substrate. Surprisingly, it is also possible to assemble multilayers of charged species on uncharged substrates.[20-22] In one recent study, charged multilayers were grown on chemisorbed hydrophobic films on a SiO_2 substrate.[23] Here, an initial adsorption of charged species at defects (uncovered SiO_2 areas) was proposed, which then would render further adsorption possible. However, such a mechanism seems impossible for the completely unpolar polypropylene which we used with good results. Apparently, the partially hydrophobized polycation **3** deposited as first layer acts as intermediary between the apolar substrate and the polyions. After deposition of hydrophobized **3** on polypropylene, the systems **PVS/1**, **PSPI/1**, **PSPM/1**, **PSS/1** and montmorillonite/**1** yield transparent, macroscopically homogeneous multilayers. In the light microscope, their appearance is also homogeneous. The visible spectra of these assemblies have the same qualitative features as the corresponding ones on glass.

The system **1**/**PSS** providing linear multilayer growth as discussed above was chosen to exemplify a quantitative comparison of multilayer assemblies on different substrates. In Figure 5, the absorbance of an assembly of **1**/**PSS** on glass is compared with the absorbance of a multilayer sample of **1**/**PSS** on polypropylene. The increase in absorbance with the number of deposition cycles is virtually the same for both substrates. Similar results are found for other polycation/polyanion combinations, such as **1**/**PVS** and **1**/montmorillonite. These results demonstrate the independence of the multilayer structure of these polyelectrolyte pairs from various substrates, suggesting a general insensitivity of polyelectrolyte multilayers to the chemical structure of the substrate chosen, if an appropriate "coupling" is assured.

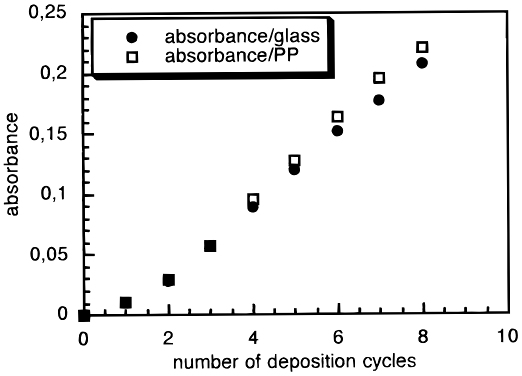


Figure 5. Comparison of the increase in absorbance with the number of deposition cycles for the system **1**/**PSS** on different substrates.

SHG Measurements

Second-harmonic generation (SHG) is forbidden in centrosymmetric systems. Hence, SHG provides a sensitive tool to study molecular organization and orientation at surfaces and interfaces.[24] For example, in the case of sharp orientational distribution of the molecules, polarization measurements can be used to determine the angle between the surface normal and one-dimensional molecules.[25]

In the first set of experiments, we investigated the second-harmonic response of various multilayer films. For these measurements, a combination of a half waveplate and a linear polarizer was used to control the incident laser intensity. The laser beam was s-polarized with respect to the sample, and all second-harmonic light was detected in reflection. In all cases, the second-harmonic signal was found to exhibit a clean quadratic dependence on the incident intensity, as expected. In the second set of experiments, the laser intensity was constant and the half-waveplate was used to continuously vary the state of polarization of the incident beam. The lineshapes of the s- and p-polarized second-harmonic signals were recorded separately. Any changes in these lineshapes are an indication of a change in the orientational distribution of the chromophores. The second-harmonic signals originated from the active layers of polymer **1** because the signals from samples made with polyelectrolytes not containing a NLO dye were undetectable using our setup.

For the second-harmonic study, we chose the systems **1**/**PVS** and **1**/montmorillonite, because they represent the extrema of the λ_{max} values of the UV/vis spectra. In the case of multilayer assemblies composed of **1** and montmorillonite, only structures terminated with montmorillonite on the top were studied because such structures are unavoidable for building multilayer assemblies. The absolute intensity of the SH signal is low in these cases, and we do not encounter the quadratic dependence of the second-harmonic intensity on the number of deposition cycles as expected for a buildup with the same degree of order in each layer. However, it has to be pointed out that the intensity of the second-harmonic signals increase with the number of layers of polycation **1**, which definitely indicates a certain degree of noncentrosymmetric ordering in every layer. The low intensity of the signal may be caused by two effects: the chromophores may be forced into an arrangement parallel to the surface layer by the rigid sheets of montmorillonite, and at the same time, they may to some extent be influenced to form antiparallel aggregates, as the $\lambda_{\max}$ of the UV/vis spectra already suggest.

The highest second-harmonic signal (about a hundred times of the intensity of a single layer of **1**/montmorillonite) was observed in the case in which only one active layer of polymer **1** was used on top of a **PVS** layer. This signal level was the same for the case in which the active layer was on the top and the case in which an additional layer of **PVS** was deposited on the top. The two polarization line shapes for these two cases were also essentially identical. These results suggest that a single layer of polycation **1** forms a noncentrosymmetric structure whose organization is not influenced by the subsequent deposition of a **PVS** layer.

These results were dramatically changed by the deposition of a single layer of **PCM** on top of the **PVS** layer. In this case, the second-harmonic signal was decreased by a factor of 20 compared to structures with no **PCM**. In addition, the polarization line shapes were also significantly changed. These results suggest that the binding of the **PCM** layer modifies the active layer of polymer **1** in such a way that the degree orientation of the chromophores in polymer **1** is significantly decreased. Therefore, a reorganization of the underlying chromophore layer must be assumed. When more double layers of **PVS**/**1** are added, a substantial second harmonic signal is still present, but it does not increase to the original single-layer level or above this level any more. Therefore, on the one hand, we may assume the anisotropy of the deposition process favors noncentrosymmetric organization of the chromophores in the system **PVS**/**1**. On the other hand, the overall degree of orientation becomes smaller with the number of deposition cycles. UV/vis spectroscopy suggests that the aggregation behavior of polycation **1** does not change throughout the assembly. So, most probably, the deposition of subsequent polycation layers creates changes in the internal field the active polycation layer experiences. As a consequence, most of the orientation of the dye moieties in the individual layers is macroscopically canceled out.

Conclusions

We synthesized a new ionene-type polycation with a high content of hydrophobic groups. A NLO dye moiety is attached to the polymer backbone which is useful for various investigations. Transparent homogeneous films consisting of polyelectrolyte multilayers from this polycation and various polyanions can be assembled not only on the usual hydrophilic, charged glass substrates but also on hydrophobic, apolar substrates such as polypropylene foil. The choice of the anionic counterpart has dramatic effects on the multilayer buildup and the UV/vis spectra of the polymer films. Therefore, an influence of the anions on the aggregation state of the dye moities in the polycation is assumed. Second-harmonic generation measurements also confirm the significantly different degree of orientation of the dye molecules in multilayers of different composition. In some cases, the anisotropy of the deposition process leads not only to a partial alignment of the chromophores but also to a partial orientation. In contrast to the usual perception of such multilayer structures, the molecular fragments are not necessarily arranged isotropically. Remarkably, a similar observation has been reported most recently for a different polyelectrolyte system, in a rapid communication which appeared during the reviewing of our study.[26] The decrease of the SHG signal which occurs in some cases when nonlinear optically inactive polycation layers are deposited on top of an existing assembly suggests a partial reorientation of the underlying layers.

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