

Reversal of Interfacial Dipole Orientation in Polyelectrolyte Superlattices Due to Polycationic Layers

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Repeated bilayers of a polycation and a polyanion were assembled by adsorption from their aqueous solutions. The polycations used were PEI (poly(ethylenimine)), PAH (poly(allylamine hydrochloride)), and generation 3.0 dendrimer (poly(propylenimine)). The polyanion was PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)-benzenesulfonamido]-1,2-ethanediyl, sodium salt]). Second harmonic generation (SHG) and UV–vis spectroscopy were used to study the structure and formation of the superlattices. The linear increase in absorbance versus the number of bilayers suggested that a uniform and consistent amount of polymer adsorbed during each deposition cycle. The observation of a second harmonic (SH) signal from the film showed that the conjugated chromophores in the PAZO polymer were aligned with a net dipole. However, the SHG signal did not continue to increase as the number of bilayers was increased. On the basis of thorough studies of the UV and SH properties for each bilayer for 10 total bilayers, we propose that the asymptotic nonlinear optical response is due to loss of charge density on the polycation. The SH signal from multilayers terminated with the polycation is smaller than when PAZO is the terminal layer. We attribute this to a change in orientation of the dipole of the outermost PAZO chromophores at the interface of the PAZO and the terminal polycation layer. We also propose multilayer assemblies that will lead to self-assembled polyelectrolyte superlattices with a high nonlinear optical susceptibility.

Introduction

Recent advances in material science have led to new developments in fast optical switching, waveguiding and chemical/biological sensing.^{1–5} Self-assembly of thin organic films is particularly promising, due to the ability to control both the structure at the molecular level and the associated physical properties. Self-assembly is a process by which hierarchical organizations are spontaneously established from the molecular level to the mesoscale. Although mesoscale ordered domains have been observed before, it is rare to see the formation of well-defined patterns up to the macroscale, especially *polar asymmetric* molecular self-assembled multilayers.^{6,7} It is more common to find apolar *symmetric* multilayer films, such as Langmuir–Blodgett films⁸ and films composed of amphiphiles adsorbed from solvents onto solid substrates.⁹ Polar asymmetric supramolecular assemblies give rise to nonlinear optical (NLO) effects that may be useful in optoelectronic devices. This work is focused on the formation and optical properties of asymmetric multilayered superlattices made by the ionic self-assembly of polycations and polyanions by adsorption from their aqueous solutions.

It is possible to create polyelectrolyte films with desired characteristics by the spontaneous adsorption of alternating layers of positively and negatively charged macromolecules.^{10–15} This layer-by-layer deposition technique has been applied to a wide variety of superlattices, from biological systems^{16–18} and polymer dyes^{14,19–21} to light emitting conjugated polymers.^{14,22,23} In particular, it is desirable to be able to control the nonlinear optical (NLO) properties and characteristics such as charge-transfer and photoluminescence. The complex relationship between the nature of the polyanionic groups, the terminal layer, and the available anchoring sites leads to different responses in the SHG. For example, Balasubramanian et al. studied 5 polyelectrolyte bilayers with an NLO active epoxy-based azobenzene polymer and observed asymptotic behavior of the SH signal after 3 bilayers.¹¹ In contrast to this, Heflin et al. reported a quadratic dependence of the square root of the SH signal of 30–100 bilayers of PAZO/PAH with measurements every 20–30 bilayers.¹² Even though many systems have been studied, the fundamental adsorption process, the conformation, and the chemical and physical properties are still not well understood. In SH studies of multilayers at the solid/liquid interface, McAloney and Goh have recently observed a fast adsorption (<10 s) of the initial polymer, followed by a slow relaxation that was attributed to conformational changes within the film.²⁴

In this work, a series of polycations are used with a common polyanion to form asymmetric polar ordered polyelectrolyte

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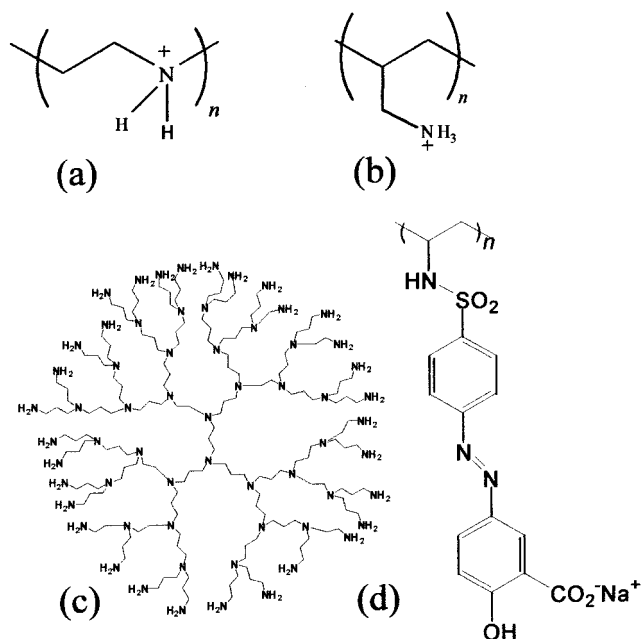


Figure 1. A schematic representation of the polycations and polyanions used to build asymmetric multilayers. The polycations are (a) PEI (poly(ethylene-imine)), (b) PAH (poly(allyl-amine hydrochloride)), and (c) the generation 3.0 dendrimer poly(propyleneimine). The polyanion (d) is PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt]).

multilayered superlattices. The polycations are PEI, PAH, and generation 3.0 dendrimer (poly(propyleneimine)). The polyanion is PAZO. The structures of PAZO and the polycations are shown in Figure 1. The PAZO contains an NLO-active conjugated chromophore with OH as an electron donor and SO₂ as an electron acceptor. The NLO-active PAZO layers are ionically sandwiched between the polycationic binder layers. The amount of adsorbed PAZO polyanion is monitored with UV-vis spectroscopy via the $\pi \rightarrow \pi^*$ transition of the azobenzene group around 355 nm. Second harmonic generation (SHG) studies are used to determine the degree of polar ordering of the chromophoric units of PAZO as a function of the number of assembled bilayers. Supramolecular structures of polyelectrolyte films for optical devices require building repeated bilayers with well-ordered dipoles and an overall nonlinear susceptibility orders of magnitude greater than that of single-crystal quartz. In this work we measure the SH response as a function of bilayer number and investigate the role of the polycationic layers in ordering the PAZO dipoles at the polycation/polyanion interface. Our results suggest that we have observed for the first time the reversal of the dipoles at this interface.

Experimental Procedure

Materials. The polycations [PEI, poly(ethylenimine); PAH, poly(allylamine hydrochloride), and a generation 3.0 dendrimer (poly(propyleneimine))] and the polyanion PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt]) were used as received from Aldrich. Ultrapure water (resistivity > 18 M Ω /cm) was used in all polymer solutions and substrate preparations. Polymer solutions were prepared at 10⁻³M (based on the molecular weight of the monomer repeat unit). All polymer solutions were used as prepared with the exception of PAH, whose pH was adjusted to 3.5. The pHs of the PEI and dendrimer solutions were neutral and 12, respectively.

Film Assembly. The films were assembled on glass substrates that were pretreated with a 70:30 solution of sulfuric acid and hydrogen peroxide for 1 h at 80 °C (piranha etch treatment). The substrates were thoroughly rinsed with deionized water and sonicated in water for 15 min to remove all traces of the piranha solution. The clean glass substrates were then immersed in the polycationic solution for 5 min at room temperature, rinsed with copious amounts of water and dried with a stream of nitrogen. The substrate was then immersed in the PAZO solution for 5 min and rinsed and dried as before. The process was repeated until 10 polycation/PAZO bilayers were assembled. Kinetic studies using UV-vis spectroscopy showed that equilibrium was established in less than 5 min for all three systems.^{25,26}

Optical Measurements. UV-visible spectra were recorded at a 1 nm resolution on a Perkin-Elmer Lambda 2 spectrometer between 320 and 700 nm and on a Cary 300 spectrometer between 255 and 700 nm. The SHG measurements were carried out in transmission geometry under nonresonant conditions using p-in and p-out beam polarizations.^{27,28,29} A mode-locked Nd:YAG laser (Continuum YG501C) provided 30 ps pulses at a repetition rate of 10 Hz for fundamental excitation at 1064 nm. The energy density at the sample was ~ 2 mJ/mm². The transmitted SHG signal at 532 nm was measured as a function of the incident angle from the normal (0°) to 64° as the sample was rotated in 1° steps under computer control.³⁰ The transmitted SHG signal was separated from the fundamental beam using a series of optical color glass filters and a 532 nm notch filter. The signal was passed through a polarization analyzer and detected using a photomultiplier tube (Thorn EMI) and gated boxcar integrator (SRS 250). The SH data points were averaged over 100 laser pulses. The SHG signal from a Y-cut quartz crystal was used as a reference.

Results and Discussion

UV-Vis Spectra. Figure 2 shows the UV-visible spectra of the three polyelectrolyte films ((a) PEI + PAZO, (b) dendrimer + PAZO, and (c) PAH + PAZO) as a function of the number of bilayers. A total of 10 bilayers were assembled for each system. A single bilayer contains a layer each of the polycation and PAZO. The maximum absorption around 355 nm increases linearly from 1 bilayer to 10 bilayers. *R*² values of 0.9956 for PEI/PAZO, 0.9979 for dendrimer/PAZO and 0.9875 for PAH/PAZO (pH 3.5) were obtained from linear regressions of the maximum absorption around 355 nm for the three systems. The absorption band around 355 nm is attributed to the (A₁) $\pi \rightarrow \pi^*$ transition in the azobenzene group of the PAZO.^{31,32} The films also showed a band near 250 nm (A_s), which is attributed to the electronic transition moment along the short axis of the *trans*-azobenzene chromophore.^{31,32} The data in Figure 2a,b were obtained on the Cary 300 and the data in Figure 2c was obtained on the Perkin-Elmer Lambda 2. The Lambda 2 did not allow absorption measurements below 320 nm. The intensity ratio A_s/A₁ is greater than 0.55 in all three films, which indicates that the azobenzene groups are polar ordered in all three systems.³¹⁻³³ Dante et al used the intensity ratio A_s/A₁ during photoisomerization in the PDDA (polydiallyldimethylammonium chloride)/PAZO system to indicate that the *trans* units of PAZO at the end of the photoreaction are oriented more perpendicular to the substrate.³¹ In our systems, neither the A_s nor A₁ bands were observed from substrates containing a single layer of the polycation (not shown). Since the strength of the $\pi \rightarrow \pi^*$ transition band increases linearly, we know that identical amounts of PAZO are adsorbed on the polycation after every adsorption cycle. Adsorption of PAZO

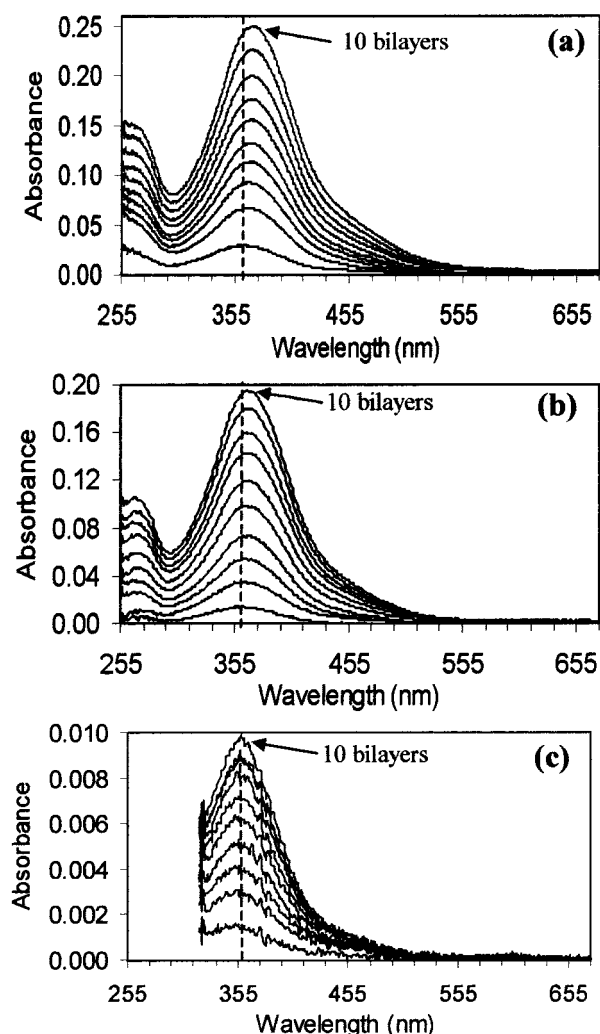


Figure 2. UV-visible spectra of the (a) PEI/PAZO layers, (b) dendrimer/PAZO layers, and (c) PAH/PAZO layers for 1–10 polycation/PAZO bilayers. A dashed line through the peak absorption of the first layer is drawn to show any shifting as the number of bilayers increases. The PAH solution was adjusted to pH 3.5 in order to observe PAZO adsorption. The absorbance maxima near 355 nm increases linearly with the number of adsorbed layers for the three systems.

was not detected in the UV-vis spectrum at pH 7 for the PAH + PAZO system. However, it was observed at pH 3.5, as shown in Figure 2. This result suggests that the adsorption is strongly dependent on the charge density of the polycation, in agreement with previous work.¹⁴ UV-vis measurements were taken for all three systems at various locations on each glass slide. These spectra were all identical indicating that the polyanion is adsorbed uniformly across the entire film.

For a given film, the structural arrangement of the PAZO may vary between the different bilayers. This is indicated by shifts in the wavelength of the A_1 band. Figure 3 shows the red shift $\Delta\lambda$ (which is the difference between $\lambda_{\max}(A_1)$ for the n th bilayer and $\lambda_{\max}(A_1)$ for the first bilayer) as a function of the number of bilayers for all three systems. The PEI/PAZO system shows the strongest red shift and plateaus to a constant value after six bilayers. Although others have observed strong blue shifts in the PEI/PAZO system beyond 10 bilayers,³¹ this is the first observation of a strong red shift between 1 and 10 layers and may indicate the formation of PAZO J-aggregates.³⁴ The dendrimer/PAZO system shows a constant red shift after the first layer. This suggests the first layer of PAZO assembles very differently from PAZO in the subsequent bilayers, indicating

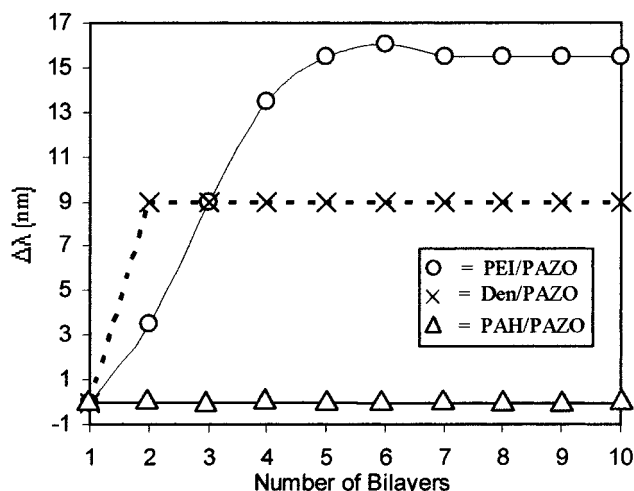


Figure 3. The shift in the $\pi \rightarrow \pi^*$ transition wavelength maximum ($\Delta\lambda$) around 355 nm as a function of bilayer number for the PEI/PAZO (○), dendrimer/PAZO (×), and PAH/PAZO (△) systems. The shifts are measured relative to the first bilayer.

that the substrate has a strong influence on the first bilayer. The observation of a blue shift beyond 10 bilayers by others for the PEI/PAZO system suggests the coexistence of H and J-aggregates.³¹ Since we do not observe any shifts in the UV-vis spectra for the PAH/PAZO system (Figure 3), we conclude that the packing mode does not change in the PAH/PAZO system as the number of bilayers increases. Figure 2 shows that PEI promotes greater deposition of PAZO compared to PAH and dendrimer. This probably reflects the different charge densities in the polycations, as well as the branching structure of the PEI.³¹

The observed red shift may also be attributed to the interaction of the polar PEI with PAZO chromophores. Since the PAZO units are conjugated, interaction with a polar species would affect the position of the $\pi \rightarrow \pi^*$ absorption band. Although PAH is also polar, a red shift is not observed in the PAH/PAZO system. Therefore, we conclude that although there is probably some interaction between the polar polycations and the PAZO chromophore, it contributes little to the observed red shift. More likely a bulk phase aggregation of PAZO is responsible for the red shift. The amount of aggregation is dependent on the polycation used in building the film.

Second Harmonic Generation. SH data were collected in transmission geometry.^{8,35–37} Figure 4 shows the SH intensity as a function of incident angle, from normal (0°) to 64° for a PEI/PAZO bilayer. The Maker fringes arise from the interference of the second harmonic signal generated from the films that are adsorbed on both sides of the glass substrate. No SHG signal is observed from just the polycationic layer. This demonstrates that the SH signal is produced from the PAZO layer, and not the polycationic layer. One would expect a significant SH response from the PAZO chromophore, since it possesses strong electron donating and accepting groups, bridged by a π -conjugated azobenzene group. A nonzero SH response indicates that the chromophores within the PAZO layer are orientationally ordered. However, the signal is significantly less than that from single-crystal quartz. If the polymer adsorbed with the chromophoric units isotropically oriented, no net SH signal would be observed. The intralayer dipole order probably arises from the electrostatic interaction between the azobenzene chromophore of PAZO and the polycation layer and would be expected to be greatest near the polycation/PAZO interface. For the p-in and p-out polarization combination used in this work,

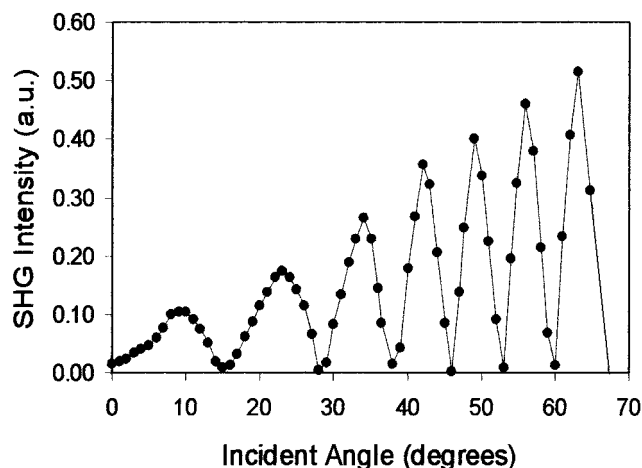


Figure 4. A typical SHG interference pattern from the polycation/polyanion film as a function of incident angle. The fringes arise from the interaction between the SH waves generated from the films on both sides of the glass substrate. The data represents a single bilayer of PEI/PAZO.

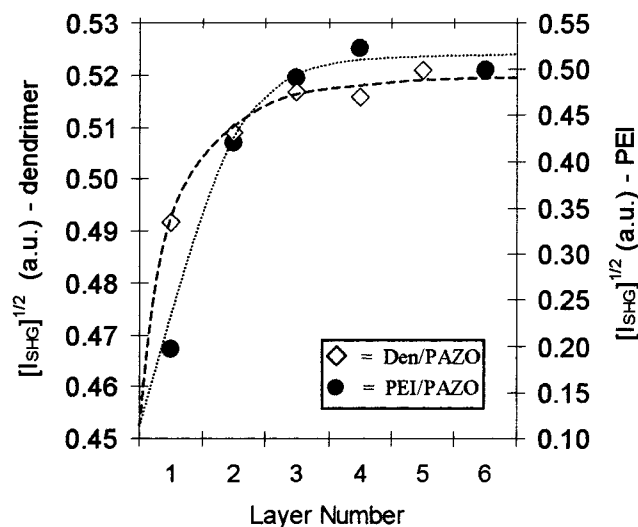


Figure 5. The square root of the SHG signal as a function of bilayer number for the PEI/PAZO system (\bullet) and the dendrimer/PAZO system (\diamond). The SH signal from both systems plateaus after a couple of bilayers. The broken lines are a guide to the eye.

the angular response of the SHG data shown in Figure 4 suggests that the overall orientation of the chromophore is close to the surface normal.^{9,27,28,30} We did not calculate the exact angle, since it likely changes with the number of bilayers. We instead focus only on the degree of orientational order within the film.

Figure 5 shows how the SH intensity varies as a function of the number of bilayers for the PEI/PAZO and dendrimer/PAZO system. The PAH/PAZO system generated very weak SH signal, comparable to the experimental noise. If the bilayers were centrosymmetric with respect to the neighboring bilayer, then the nonlinear second harmonic response would cancel due to destructive interference. Thus, a strong and weak SH relationship would result for odd and even number of bilayers, respectively.⁸ Others have also observed a nonzero SH signal, indicating that PAZO layers are noncentrosymmetric and polar ordered within a polyelectrolyte multilayer system.^{31,38} Figure 5, however, does not show the expected quadratic variation, but instead the SHG signal increases for the first few bilayers and then plateaus. The flat region could be interpreted as either a region of no further PAZO adsorption or as a region where no additional order in the film is gained by subsequent PAZO layers. The UV-vis

spectra (Figure 2) eliminate the first possibility since absorbance increases linearly from 1 to 10 bilayers. We conclude that the loss of polar order in the PAZO chromophores is caused by the reduction in charge density of the underlying polycation layer. As the number of polycation layers increases, the overall charge density of the polycation decreases on the surface due to the exclusion of hydrophobic polymer backbone from the underlying electrostatic interface.¹¹ Thus, the PAZO layer adsorbed on the polycation will be less ordered as the number of bilayers increases. This reduction in charge density is not large enough to cause a noticeable change in the amount of adsorbed PAZO, but enough to decrease the orientational order of the PAZO chromophores. Even if there were a slight reduction in the amount of PAZO adsorbed, this would have little effect on the SHG data since polar order is thought to arise predominately at the polycation/PAZO interface. The limit of interfacial disorder in the PAZO layer seems to be reached within a few bilayers. Since two different polycations (with different charge densities) were used, the SHG intensity saturated at different bilayer numbers. This is strong evidence that the charge density of the polycationic layers is responsible for the asymptotic SHG response.

The behavior of the SH signal as the number of bilayers increases is in sharp contrast with the quadratic dependence observed by Heflin et al.¹² However, Heflin et al. studied 30–100 bilayers of PAH/PAZO, while our films are comprised of 1–10 bilayers. Our results are consistent with studies on an epoxy-based azobenzene system by Balasubramanian et al., who observed an asymptotic SH signal after 3 bilayers.¹¹ This suggests that this asymptotic behavior after a few bilayers is general for many different polyelectrolyte systems. If we can maintain the charge density of every polycation layer comparable to that of the glass substrate, we should be able to form superlattices that have large $\chi^{(2)}$ coefficients and produce a quadratic SHG response. An inorganic clay layer of high charge density sandwiched between the polycation layers might achieve this goal.³⁹ This would allow the subsequent polycation layer to interact with more PAZO chromophores, yielding an overall dipole similar to the first PAZO layer. We are currently investigating using Laponite to do this.

Displacement of counterions from within the interfacial electric double layer (the Stern layer) makes the adsorption of the polymer entropically favorable. The role of water in the adsorption mechanism must also be considered. It is well-known that water plays an important role in the thermodynamics of the self-assembly of films and micelles.⁴⁰ For example, the hydrophobic effect is driven by the displacement of an ordered clathrate cage of water molecules around hydrocarbon chains resulting in a large entropy gain. In recent SHG studies of PSS-(polystyrene sulfonic acid)/PDDA multilayers, McAloney and Goh found that a multilayer of ordered water molecules exists above the polyelectrolyte film that contributes to a strong SH signal via the third-order nonlinear susceptibility.²⁴ Since our films are adsorbed from aqueous solutions, we may also have an ordered surface water structure. The polymer absorption onto the water may have an adsorption mechanism similar to that of the hydrophobic effect. The fact that there is no reduction in the amount of adsorbed PAZO on polycationic layers with decreasing charge densities suggests that the driving force behind adsorption may be the entropy gain in displacing not just the counterions, but also the ordered water molecules on the polycation. Since the amount of PAZO adsorbed remains constant for all the multilayers, this could indicate that the

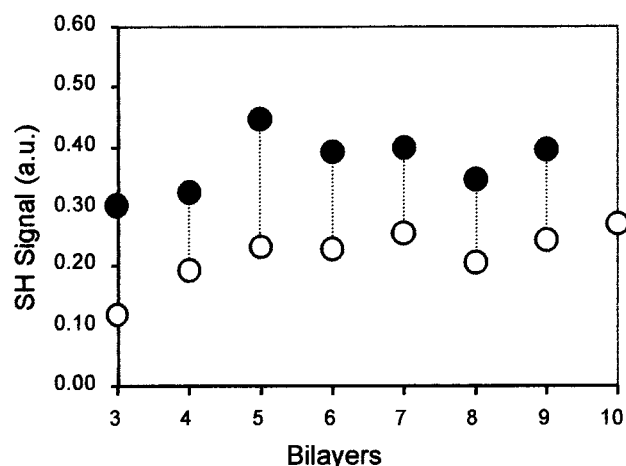


Figure 6. SHG intensity as a function of the number of layers. Filled circles (●) represent the SH response from films containing PAZO as the outer layer and open circles (○) represent the SH response from films containing PEI as the outer layer. This pattern indicates a change in chromophore orientation within PAZO layers that results in dipole reversal. The lines are to guide the eye.

amount of water adsorbed onto the polyelectrolyte may be independent of the amount of polycation.

Figure 6 shows the SH intensity as a function of the number of bilayers for the PEI/PAZO system. The first open circle represents the signal generated from the 2(PEI/PAZO)/PEI film. The first filled circle represents the 3(PEI/PAZO) film, and so on. Thus, all open circles represent PEI as outer layers, and all filled circles represent PAZO as outer layers. The data in Figure 6 shows that systems containing PEI as the outer layer generate less SH signal than those containing PAZO as the outer layer. This reduction in SH signal could be due to the displacement of PAZO by the PEI during adsorption. However, the UV spectra of films terminated with PAZO are identical to those terminated with the polycations. This shows that the polycations do not displace any previously adsorbed PAZO on the solid substrates during the adsorption process.

To confirm that the reduction in SH signal was due to the polycation, a common PEI/PAZO bilayer was made and then was terminated with the three polycations: PEI, dendrimer, and PAH. The SHG data for these *trilayer* systems is shown in Figure 7. The data are shown for five SH Maker fringe maxima. When the polycation is the terminal layer, all three systems show an appreciable attenuation of the SH signal. Since we observe no reduction in the amount of PAZO adsorbed, the decrease in the SH signal must be caused by a change in the ordering of the PAZO chromophore dipole due to the polycation outer layer. In a polycation/PAZO system, the polycation aligns the internal dipoles of PAZO (Figure 8a). However, if PAZO is sandwiched between two polycation layers, there will be on average a very small net dipole. The outermost polycationic layers will cause the PAZO dipoles at the interface to reorient in the opposite direction thus causing partial cancellation of the observed SH signal. (Figure 8b). Therefore, the PAZO terminated layers will always give larger SH signals than those capped with the polycation. This effect is analogous to the reversal of the SH phase by an applied electric field.⁴¹ This is the first demonstration of an interfacial dipole reversal in polyelectrolyte films. By inserting uncharged spacers between the polycation and the PAZO, we may be able to eliminate the interfacial dipole reversal and produce films with a larger SH response. We note that other outer layer dependencies have been observed in related polyelectrolyte systems by others using fluorescence spectroscopy,

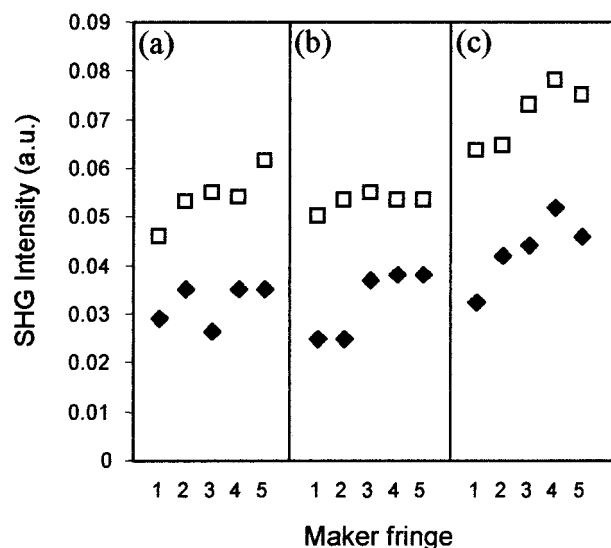


Figure 7. SHG intensity from trilayer systems composed of PEI/PAZO as a common initial bilayer, followed by (a) PEI, (b) dendrimer, and (c) PAH as a terminal layer. The data are shown for five of the Maker fringes. Filled data points (◆) represent the SH response from films containing the polycation as the outer layer and open data points (□) represent the SH response from films containing PAZO as the outer layer.

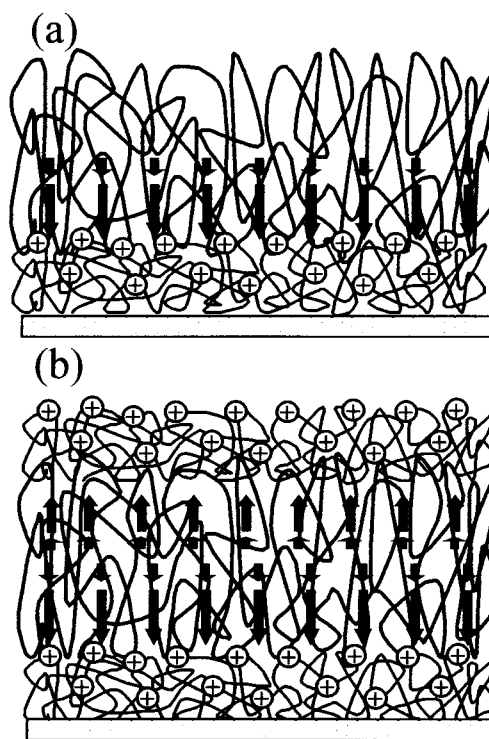


Figure 8. Schematic of the polyelectrolyte film showing the arrangement of the PAZO dipoles near the polycation/PAZO interface. In (a) the film contains PAZO as the outer layer with strongly oriented dipoles at the polycation/PAZO interface. The orientational order decreases further from this interface. In (b) the film contains the polycation as the outer layer. The orientation of the PAZO chromophores at the outermost polycation/PAZO interface are opposite of those at the initial interface. The effect of adding a terminal polycation is a decrease in the overall noncentrosymmetry of the PAZO layer.

copy, but these trends were not explicitly attributed to dipole changes. For instance, Caruso et al. observed how the ζ -potential of the films was altered by the adsorption of PAH or PDADMAC (polycations) on PSS (polyanion).⁴² Adsorption of a polycation caused an increase ($\sim +60$ mV) in the ζ -potential.

Subsequent adsorption of the polyanion caused a significant decrease (~ -60 mV). This effect persisted for 11 monolayers. They attributed the reversal in ζ -potential to conformational shifts within surface polyelectrolyte layers. However, we believe that these conformational changes could be the result of dipole reversal, similar to what we have observed in this work.

Summary

For a series of polyelectrolyte systems containing PAZO as the NLO-active polyanion, we have shown through SHG studies that the dipoles are ordered at the interfacial region of the polycation/PAZO bilayers. Studies undertaken with a polycation outer layer reveal a change in chromophore orientation at the polycation/PAZO interfacial region that results in dipole reversal and leads to an attenuation of the SH signal when the polyelectrolyte film is terminated with a polycation. Controlling charge density and eliminating dipole reversal will aid in the construction of new asymmetric superlattices with large nonlinear optical coefficients and SH signals that increase with number of layers.

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