Azo Chromophore-Functionalized Polyelectrolytes. 2. Acentric Self-Assembly through a Layer-by-Layer Deposition Process

Srinivasan Balasubramanian, Xiaogong Wang, Hsing Chia Wang, Ke Yang,[†] Jayant Kumar,[†] and Sukant K. Tripathy*

Departments of Chemistry and Physics, Center for Advanced Materials, University of Massachusetts—Lowell, Lowell, Massachusetts 01854

Lian Li

Molecular Technologies Inc., Westford, Massachusetts 01886

　　　We have developed epoxy-based, water-soluble azo polymers containing ionizable groups in the azobenzene functionality. We describe a novel approach of the noncentrosymmetric self-assembly of azobenzene chromophores in these polymers through a layer-by-layer deposition technique. The polymers in solution function as polyelectrolytes and were assembled into multilayers by alternately depositing the ionic azobenzene polymers and commercially available polyelectrolytes of the opposite charge on glass substrates. The chromophores in the multilayer film self-assemble into a noncentrosymmetric order requisite for exhibiting second-order NLO property. NLO coefficients are comparable to the poled, spin-coated films of the same polymer. The self-organization of the chromophores was further verified using transmission electron microscopic (TEM) and electroabsorption spectroscopic studies.

Introduction

　　　Azobenzene-functionalized polymeric materials have been investigated for a long period[1] and have attracted significant renewed attention for over a decade.[2−6] Potential applications such as electrooptic modulation,[7,8] and information storage,[9−11] among others, have been the motivation behind the intense recent activity in this area. During the past decade a wide variety of functionalized polymers with chromophores in the main chain or in the side chain have been synthesized.[12,13]

　　　A number of polymeric systems where the NLO chromophores are present as "dopants" (guest−host systems)[14,15] or as part of the polymer chain[16−18] have been reported. To realize second-order optical nonlinearity in a system, the NLO chromophores have to be aligned into a noncentrosymmetric arrangement.[7] This can be achieved by electric field poling.[19,20] However, in poled polymeric systems the chromophores exist in a thermodynamically unstable state.[5] Over a period of time the chromophore orientation randomizes to an equilibrium distribution resulting in the decay of NLO response. Incorporation of the chromophores in a polymer matrix and cross-linking the polymer after poling[21−23] are among some of the strategies that have

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been developed to address this problem. Though systems that possess high temporal stability have been developed, chromophore randomization still persists as a major hurdle in the development of practical materials and devices.

Processes in which the chromophores self-organize into a noncentrosymmetric alignment have been envisioned as attractive alternatives to the forced ordering of the chromophores. Relatively few methodologies that involve the self-assembly of the chromophores into an acentric order have been reported. One of the approaches involves the formation of acentric Y-type LB films incorporating NLO chromophores.[24,25] Though the LB technique can lead to well-ordered structures, the process of thick film growth is tedious, films formed are often fragile, and the chromophore alignment is not usually stable. Other interesting approaches for the formation of multilayers through chemisorption processes have been reported.[26-29] Katz and co-workers have reported the formation of multilayers containing NLO chromophores through sequential phosphorylation and zirconation.

Work carried out in our laboratory on post-azo functionalization on polymers has proved to be a versatile synthetic tool in the development of novel azobenzene-containing polymers. Azobenzene-functionalized polymers containing heteroaromatic groups, azobenzene-functionalized polydiacetylenes, and water-soluble, epoxy-based azobenzene-incorporated polyelectrolytes have been synthesized using the post-azo-coupling reaction.[30-32] The water-soluble azobenzene polymers provide an opportunity to develop thin films with interesting electrooptical properties through a layer-by-layer deposition process recently developed by Decher and co-workers.[33] This novel thin film fabrication process, involving the layer-by-layer deposition of oppositely charged polyions,[34-36] has been utilized in the fabrication of a wide variety of electroactive materials, including conjugated polymers[37] and poly(phenylenevinylene) precursor polymers.[38] In our initial studies[39] we have observed the layer-by-layer deposition process to introduce acentric polar order and hence second-order optical nonlinearity.

The side-chain epoxy-based azo polymers synthesized in our laboratory were designed to contain ionizable groups in the chromophores. Under appropriate pH conditions, the polymers behave like polyelectrolytes. Using these polyelectrolytes along with oppositely charged polyelectrolytes, multilayer thin films were fabricated through the layer-by-layer deposition process. The multilayers formed were uniform and of excellent optical quality. The films exhibit second-order NLO response comparable to and in one case even better than the corresponding poled spin-coated films. Second-harmonic generation from the multilayer films indicates that the chromophores exist in a noncentrosymmetric arrangement in the multilayer films. Transmission electron microscopy (TEM) studies indicate that the chromophores self-assemble into an ordered structure in the bilayer and multilayer films during the film fabrication. The orientational order of the chromophores was further confirmed with electroabsorption spectroscopy.

Experimental Section

Materials. Frosted glass slides used as substrates for multilayer fabrication were purchased from VWR Scientific. The reagent used for cleaning the glass slides, Chem-Solv Lab cleaner, and Collodion solution, used in transmission electron microscopy studies, were obtained from Mallinckrodt. Water from an Elix 10 water purification system from Millipore Corp., which is capable of providing deionized water with >15 MΩ resistance, was used in the multilayer fabrication process.

Polymer Synthesis. The general synthetic scheme is shown in Figure 1. All five polymers were synthesized by the post-azo-coupling reaction. The synthetic details and characterization of the polymers are reported in paper 1 of this series.[32]

Multilayer Fabrication. Multilayers were assembled on glass slides whose surfaces were rendered hydrophilic by the following procedure. The glass slides were sonicated in Chem-Solv solution for 1 h followed by rinsing with MilliQ water several times. The slides were then dried. Multilayer films of the polymers CH-1A-CA, CH-1A-NS, and CH-1A-PY were fabricated with the appropriate polyelectrolyte carrying the opposite charge. In the case of the polymers CH-1A-Sm and CH-1A-Sp, the films fabricated were of poor optical quality. The polymer BP-1A-CA reported in paper 1 of this series is insoluble in water over a wide pH range and hence could not be fabricated into multilayer films. In the case of CH-1A-PY, sulfonated polystyrene (SPS) was used as the polyanion and the pH of the two solutions was maintained at 2.5. In the case of CH-1A-CA and CH-1A-NS, poly(diallyldimethylammonium chloride) (PDAC) was used as the polycation and the pH of all the solutions was about 8.0. In a typical experiment the slide was dipped alternately in the polycation and polyanion solutions for 10 min each with a MilliQ water (of same pH) rinse in between. The concentration of the two solutions was 0.5 mM based on the repeat unit weight. Bilayer formation was monitored using UV–vis spectroscopy. The slides were dried after each bilayer deposition, and the absorption spectrum was recorded. The thicknesses of the multilayer films were measured using an AutoEL-III automatic ellipsometer (Rudolph Research) with a He–Ne laser (632.8 nm).

Nonlinear Optical Property Measurement. The second-order NLO coefficients (d_{33}) of the self-assembled films and spin-coated, poled films were measured by second-harmonic generation (SHG) using 1.064-μm laser radiation. The measurements were carried out on a Q switched Nd:YAG laser (Quantel 660A). The SHG signal, selected with an interference

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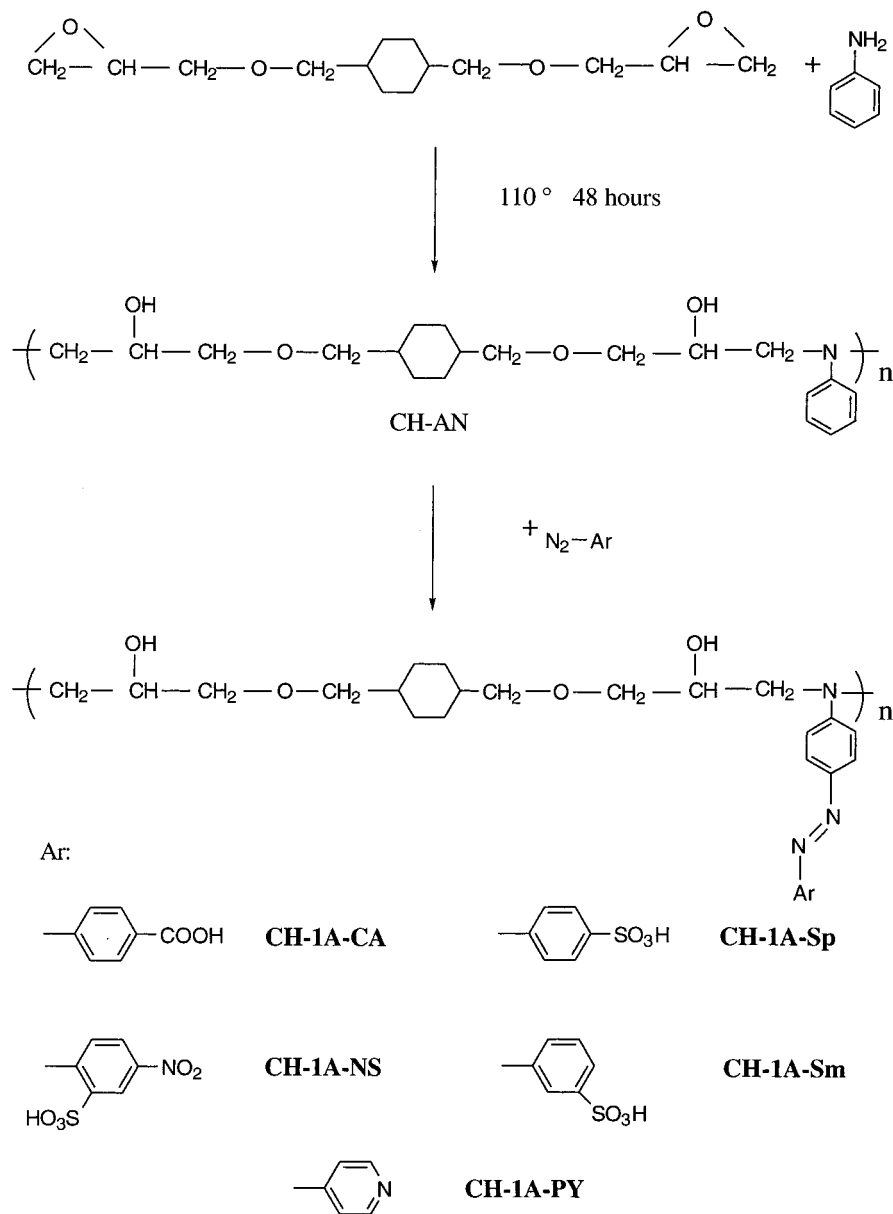
Figure 1. Synthesis of epoxy-based azo polymers through the post-azo-coupling reaction.

filter at 0.532 μm, was detected by a photomultiplier tube and measured with a boxcar integrator. A Y-cut quartz with d_{11} = 0.49 pm/V (at 1.064 μm) was used as the reference. By comparing the SHG intensity from the multilayers with that from the quartz crystal, the d coefficients of the sample were determined.

Transmission Electron Microscopy Studies. The substrates were prepared by cleaning the glass slides ultrasonically in Mallinckrodt Chem-Solv Lab cleaner and then dipping into diluted collodion solution. The collodion-covered glass slide was dipped into polycation solution and then rinsed with water. This was followed by dipping into polyanion solution and then rinsing with water. The adsorption of the polymeric ions on collodion film was monitored using UV−vis spectroscopy. The process was repeated several times to form mutilayers. The films on the surface of the glass slide were scratched and dipped into water. The collodion film with the multilayers was separated from the glass substrate by floating the scratched end of the film and stripping in water. The films were picked up by 400 mesh bare copper grids. Collodion was removed by exposing the film to amyl acetate vapor. This was achieved by placing the copper grid containing the film on a filter paper supported by a steel mesh just above the amyl acetate solution. Collodion was dissolved completely and

extracted away after exposure to the vapors for 6 h. The multilayer films on bare copper grids were observed by TEM.

The TEM observations were carried out by using a Philips 400 STEM operated at 120 kV. The low dose unit for EM 400 was used to reduce radiation damage by the electron beam. Selected area electron diffraction patterns (SADP) were calibrated by using Au standard sample.

Electroabsorption Spectroscopic Studies. For the electroabsorption studies, ITO (indium tin oxide)-coated glass slides were used as substrates. The slides were cleaned by sonicating in 5% Lysol solution for 30 min (appears to work quite well) followed by rinsing repeatedly in water. A 50-bilayer film of PDAC/CH-1A-NS was formed on the ITO-coated glass substrate. The concentrations of the polycation and polyanion were maintained at 0.5 mM and pH 8. The multilayer film was dried overnight in a vacuum oven, and a 300-Å layer of aluminum was deposited on the surface of the film. A sinusoidal electric field (f = 1 kHz, V_{p-p} = 25.5 V) was applied to the sample. A beam of p-polarized light from a tungsten lamp through a monochromator was incident on the sample with the angles of incidence 67° and 0° (θ_0 = 0° for normal incidence). The electroabsorption signal ΔI, which is defined as the change in the output intensity I, was detected by a lock-in amplifier set at twice the electrical modulation
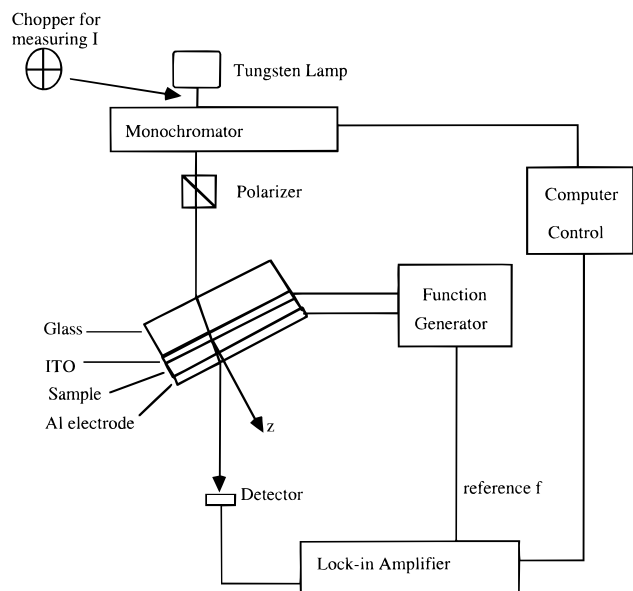
Figure 2. Experimental setup for electroabsorption measurement.

frequency (2*f*). The sign of ΔI was determined by comparing the amplified signal from the lock-in amplifier at 2*f* and the reference signal from the function generator on an oscilloscope. The output intensity *I* (without the electric field) was measured. A computer was used to synchronize the change of wavelength of the monochromator and the data reading of the lock-in amplifier. The experimental setup is shown in Figure 2.

A film of CH-1A-NS was spin-coated from its DMF solution on an ITO-glass substrate for comparison. A 300-Å thick aluminum film was deposited on the spin-coated film by thermal evaporation. The electroabsorption measurements were performed from 430 to 750 nm for the multilayer self-assembled film and from 540 to 750 nm for the spin-oated film of CH-1A-NS, with the angle of incidence 0° and 67° for both films. The dispersions of the real and imaginary part of the complex refractive index, $\tilde{n} = n + i\kappa$, of the multilayer film and the spin-coated film of CH-1A-NS were measured using an ellipsometer (Rudolph Research, type 43603-200E) and a UV−vis spectrometer (Perkin-Elmer Lambda 9). The results of $\Delta I/I$ and the complex refractive indices are used for the calculation of third-order nonlinear optical susceptibility components $\chi^{(3)}_{1133}$ and $\chi^{(3)}_{3333}$.

Results and Discussion

An epoxy-based polymer was synthesized by reacting aniline with 4-cyclohexanedimethanol diglycidyl ether. The molecular weight of the precursor polymer as measured by gel permeation chromatography was M_n = 3000 and M_w = 4500, relative to polystyrene standards. Ionic azo chromophores were introduced in the polymer chain through the post-azo-coupling reaction. Details of synthesis and characterization are provided in paper 1 of this series.[32] The degree of functionalization was determined to be about 100% by ^{1}H NMR spectroscopy.[32] The ionic groups aid in the solubility of the polymers in water and in the multilayer fabrication process. Polymers CH-1A-CA and CH-1A-NS are soluble at pH 5.0 and above. The polymer CH-1A-PY is soluble in water only at low pH (below pH 2.5). The UV−vis spectra of the polymers CH-1A-CA, CH-1A-NS, and CH-1A-PY in DMF are shown in Figure 3.

The azo polymers can be combined with commercially available polycations and polyanions such as poly-
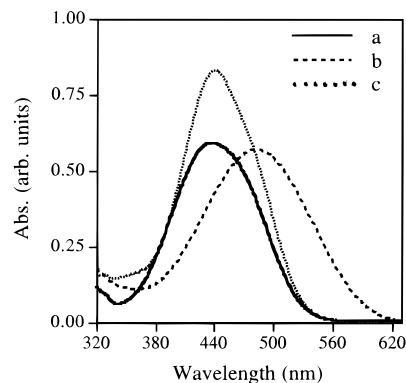

Figure 3. Absorption spectrum of (a) CH-1A-CA, (b) CH-1A-NS, and (c) CH-1A-PY in DMF solution.
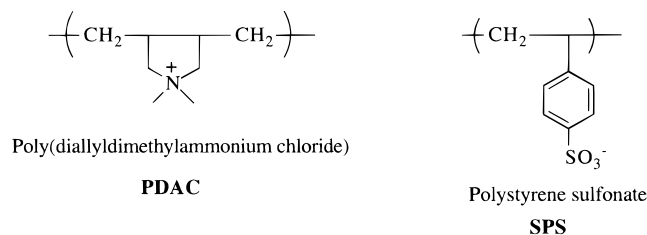

Poly(diallyldimethylammonium chloride)

PDAC

Polystyrene sulfonate

SPS

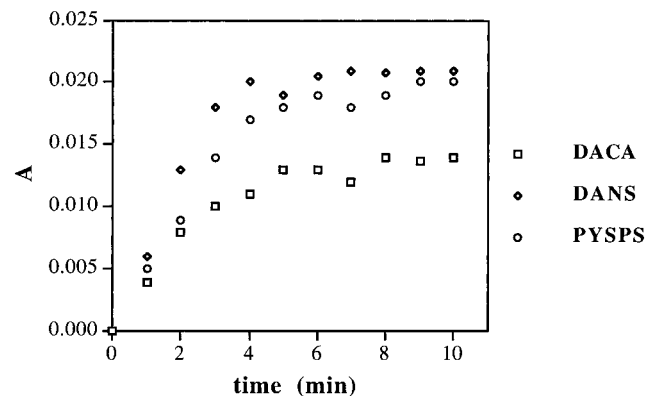**Figure 4.** Polycations and polyanions for multilayer fabrication.

Figure 5. Absorption as a function of deposition time for a single bilayer film.

Table 1. Polycation/Polyanion Combinations for Multilayer Fabrication

sample	polycation	polyanion
DACA	PDAC	CH-1A-CA
DANS	PDAC	CH-1A-NS
PYSPS	CH-1A-PY	SPS

(diallyldimethylammonium chloride) (PDAC) and sulfonated polystyrene (SPS) (Figure 4) to form various kinds of multilayers. The combinations of polycation and polyanion used to form multilayer films are indicated in Table 1. Multilayers were formed through a layer-by-layer deposition process on hydrophilic glass slides. The film quality depends on the solution concentration and pH. The deposition process was monitored using absorption spectroscopy. The absorption of a single bilayer formed was measured as a function of time and is displayed in Figure 5. From Figure 5 it can be observed that the deposition process saturates after about 7 min. A dipping time of 10 min in each polyelectrolyte solution was used for all the multilayer fabrication processes.
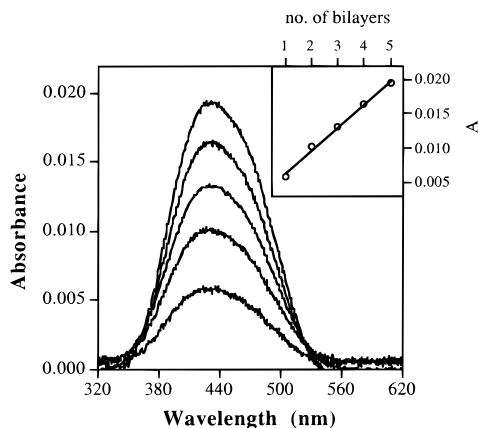
Figure 6. Absorption spectra of five-bilayer DACA film (inset: linear growth of adsorption).
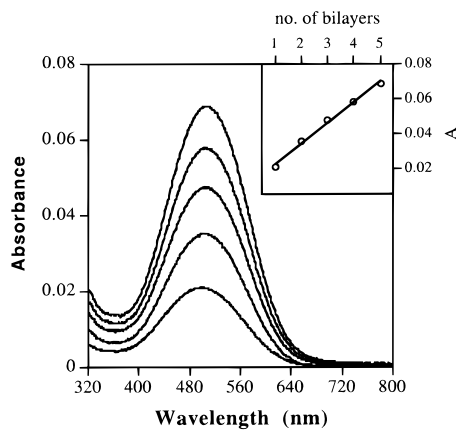

Figure 7. Absorption spectra of five-bilayer DANS film (inset: linear growth of adsorption).

For PDAC/CH-1A-CA multilayers, the concentrations of both the solutions were maintained at 5×10^{-4} M based on the repeat unit weight. The pH of the solutions was adjusted to about 8.0. The glass slide was first dipped in the PDAC solution for 10 min followed by rinsing with MilliQ water of the same pH. It was then dipped in the CH-1A-CA solution for 10 min followed by rinsing with MilliQ water of pH 8.0. The UV−vis spectrum was recorded after drying the slide with a stream of nitrogen gas. The process was repeated five times to assemble five bilayers on the glass slide. The UV−vis spectra of the bilayers are shown in Figure 6. The linear increase of absorption with increasing number of bilayers (inset) indicates the uniformity of the multilayer fabrication process. The thickness of the five bilayers was measured to be 80 Å using ellipsometry.

PDAC/CH-1A-NS multilayer film was prepared by a similar procedure mentioned above. Figure 7 shows the UV−vis spectra of the bilayers, and the inset shows the linear increase of the absorption with the increase in the number of the bilayers. Ellipsometry measurements indicated a film thickness of about 120 Å.

For the CH-1A-PY/SPS multilayer film, CH-1A-PY was used as the polycation and SPS as the polyanion. The film fabrication process was the same as that above. Figure 8 shows the UV−vis spectra of the bilayers. The reason for the skewed shape of the spectral curve for the first bilayer is not known. It may be due to conformational or orientational effects. Subsequent bilayer
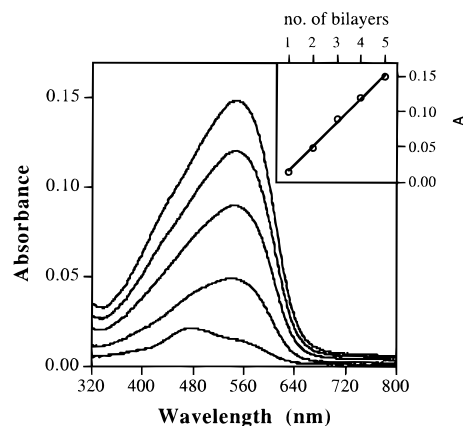

Figure 8. Absorption spectra of five-bilayer PYSPS film (inset: linear growth of adsorption).

Table 2. Second-Order NLO Coefficients of Poled, Spin-Coated Films and Five-Bilayer Films

	d_{33} (pm/V)	
sample	poled film	five-bilayer film
CH-1A-CA	27	19
CH-1A-NS	5	20
CH-1A-PY	20	6

spectra are similar in shape to each other and are similar in shape to the solution spectrum of the protonated azo polymer. The inset shows a linear increase of absorption with the number of bilayers. The five-bilayer film thickness was found to be 170 Å using ellipsometry.

Spin-coated films of the three polymers were prepared from DMF solutions for comparison with the multilayer films. The thickness of the spin-coated films was in the range of 0.4−0.5 μm.

Nonlinear Optical Property Measurement. The d_{33} coefficients of the five-bilayer films and the corresponding poled, spin-coated films are given in Table 2. As can be seen from the table, the NLO coefficients of the CH-1A-PY and CH-1A-CA polymer multilayer films are comparable to those of the poled films of the respective polymers. In the case of polymers containing the sulfonic acid functionality, CH-1A-NS, CH-1A-Sm, and CH-1A-Sp, the electric field-induced orientation of the chromophores was inefficient resulting in low (for CH-1A-NS) or insignificant (for CH-1A-Sm and CH-1A-Sp) NLO coefficients. This difficulty in poling is probably arising out of the strong interaction between the chromophores through possible zwitterionic structures. In the case of the multilayer films of the polymer CH-1A-NS, however, the chromophores efficiently self-assemble into a noncentrosymmetric order resulting in a large NLO coefficient. Poor optical quality of the multilayer films of the polymers CH-1A-Sm and CH-1A-Sp rendered measurement of the SHG signal difficult.

Through the multilayer deposition process we have developed a new strategy to fabricate second-order nonlinear optical materials without the application of large electric field.[39] The successful fabrication of an acentric multilayer film through a simple alternate deposition into aqueous solutions can potentially be extended to the formation of films with several multilayers. For this purpose, the second-harmonic response
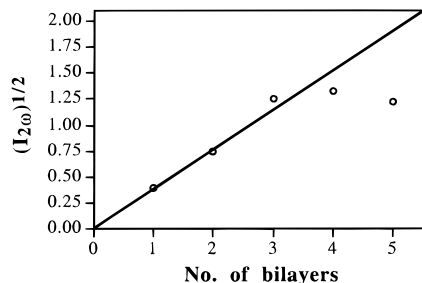
Figure 9. Square root of SHG as a function of the number of bilayers for PDAC/CH-1A-CA film.

with increase in the number of bilayers (up to five) was studied. The results obtained from SHG measurements indicate that the SHG signal increases up to three bilayers beyond which the behavior is erratic as seen in Figure 9. This indicates that the self-organization of the chromophores into an acentric order, while occurring systematically in the initial few bilayers beyond that ordering, in the film is erratic. After repeating these experiments several times, we attribute this observation to the structural feature of the azobenzene chromophore-functionalized polymer. The polymers contain nonionic hydrophobic functional groups in addition to the ionic azobenzene moieties.

While Coulomb interaction between charged azobenzene groups with the charged species on the substrate will drive these groups together, the hydrophobic groups will tend to be excluded from the substrate surface. This forms the basis for the acentric order in these bilayer films. However, this also leads to a gradual decrease in the surface charge density as the number of bilayers increases. The ordering of azobenzene chromophores observed within the bilayer is believed to be enhanced due to the interaction among the rigid-rod-like chromophores. The ordered arrangement is frozen as the anionic chromophores are anchored on the polycationic substrate due to electrostatic attraction between the substrate and the azo polyelectrolyte in solution leading to the bilayer formation. The azobenzene chromophores that are not anchored on the substrate would possess no particular orientational order in the film. As the charge density decreases with increasing number of bilayers, there will be a lesser number of anchoring sites on the substrate. This in turn leads to decreased structural ordering.

Control of charge distribution, density, and placement on the main chain and side group provides a number of approaches for optimizing the ordering process and is a subject of current study in our group. One approach involves the use of azobenzene-functionalized poly-(acrylic acid) to increase charge density and distribution on the chain. More details on the NLO property of multilayer films of this polymer will be reported elsewhere.

Transmission Electron Microscopy Studies. The morphology of the PDAC/CH-1A-NS multilayer film was studied using transmission electron microscopy. The multilayer films of good optical quality with no aggregation or holes can be formed by this technique as observed using TEM micrographs. A representative diffraction pattern from the film is shown in Figure 10. A diffused ring pattern was observed with a *d* spacing of 4.7 Å. This is attributed to the self-assembly of the azo chromophores into ordered domains normal to the

Figure 10. Electron diffraction pattern from six-bilayer PDAC/CH-1A-NS film.

film plane due to van der Waals interaction between the chromophores. Self-organization of azobenzene chromophores into liquid-crystalline domains has been reported.[41,42] Further detailed investigations of molecular organization in the multilayer films using TEM are in progress and will be reported in a separate paper.

The results from the TEM studies and second-harmonic measurements indicate that the chromophores self-assemble into a noncentrosymmetric order during the layer-by-layer deposition process at least in the first few bilayers of these polymer systems. The self-assembly of azo chromophores in a preferred order normal to the plane of the substrate was further confirmed using electroabsorption spectroscopy.

Electroabsorption Spectroscopic Studies. In this method the third-order nonlinear optical coefficients $\chi^{(3)}_{1133}$ and $\chi^{(3)}_{3333}$ are measured as a function of wavelength.[43] The conjugated mesogenic rigid chromophores are the major contributors to this nonlinearity. The ratio of the coefficients is a measure of the net orientation of the chromophores according to eq 1.[43] For an isotropic film (with random orientation of the chromophores) the ratio of the coefficients is equal to 3. In the case of spin-coated films where the anisotropic rod-like chromophores tend to lie along the plane of the substrate due to the centrifugal forces during the

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high-speed spinning process, the ratio $\chi^{(3)}_{3333}/\chi^{(3)}_{1133}$ may be significantly less than 3 for a high degree of in-plane distribution. If the chromophores are predominantly normal to the substrate, the ratio will be greater than 3.

$$\chi^{(3)}_{3333} = 3\chi^{(3)}_{1133}, \text{ isotropic film} \qquad (1)$$

$\chi^{(3)}_{3333} < 3\chi^{(3)}_{1133}$, chromophore preferentially
oriented along the plane

$\chi^{(3)}_{3333} > 3\chi^{(3)}_{1133}$, chromophore preferentially
oriented normal to the plane

To investigate the preferential orientation of the chromophores in the multilayer films, two samples were prepared. A spin-coated film of the polymer CH-1A-NS from DMF solution and a 50-bilayer PDAC/CH-1A-NS film were fabricated on ITO-coated glass substrates. A thin layer of aluminum (300 Å) was deposited on the surface of the films. The ratio of the dispersions for the multilayer film was measured to be about 4. This result indicates that the chromophores even in a 50-bilayer film maintain a net preferential orientation normal to the plane of the substrate.

In the case of the spin-coated film, the ratio was determined to be 1.9 which implies that the orienta-tional order is predominantly along the plane of the substrate. The details of the electroabsorption measurement results will be discussed in a subsequent paper in this series.[44]

In conclusion we have designed several new water-soluble azo polymers that can be processed into multi-layer films where the chromophores self-assemble into an acentric order. The self-assembly was achieved by a simple layer-by-layer deposition process without any external field. The acentric orientational order extends to several bilayers and appears to be driven by the charge distribution on the polymers and the mesogenic character of the chromophores. We are currently investigating the structure−property relationships of various ionic, water-soluble azo polymers. By the appropriate NLO polyelectrolyte design, coupled with proper control of the depositing conditions such as solution concentration and pH, among others, materials with important optical and electronic properties can be developed.

CM9707418