

Ordered Films by Alternating Polyelectrolyte Deposition of Cationic Side Chain and Anionic Main Chain Chromophoric Polymers

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Using the method of aqueous solution alternating polyelectrolyte deposition (APD), second-order nonlinear optical (NLO) polymer films were prepared for the first time in which both polymers were NLO-active. Films were prepared by alternately coating a solid substrate with an NLO-active side chain polycation and an NLO-active main chain polyanion. This new polyanion was comprised of α -cinnamoyl chromophores in the syndioregic configuration (an "accordion" polymer). The new polycation was derived from polyepichlorohydrin that was completely substituted with new stilbazolium side chain. The films were transparent and had no texture when observed by polarized microscopy. The increase in intensity of the second harmonic (SH) signal generated in the films was quadratic with each molecular layer to 20 layers. Beyond that, the SH signal intensity saturated as more layers were added.

Introduction

Alternating polyelectrolyte deposition (APD) is a new room-temperature method for the layer-by-layer fabrication of polymer films. APD has been under development now for about a decade and was pioneered by Decher's group.¹ Multilayer films are built-up by continuously dipping the substrate back and forth between the poly(cationomer) and poly(anionomer) solutions, usually with intervening rinsing and drying steps. The thickness of a polymer layer absorbed in one dipping operation is typically in the range of 0.5–2 nm.^{2,3} Compared to the Langmuir–Blodgett–Kuhn (LBK) method, by which at most a few substrates at a time can be coated, the exciting advantage offered by the APD method is that many more substrates of various sizes and shapes can be coated simultaneously in an automated process. For example, a programmable slide stainer is convenient for coating up to 50 substrates at one time.

APD is now being intensely investigated as a new method for fabricating second-order nonlinear optical (NLO) films, i.e., noncentrosymmetric chromophoric films useful in high-frequency, high-bandwidth optical switches and modulators.⁴ Several groups have recently reported fabricating thin NLO films by the APD

method.^{5–8} These studies are related to and preceded by more time-consuming covalent assembly methods^{9,10} and hybrid APD surface-activation methods.¹¹ Fabrication of NLO films by pairwise deposition of polyelectrolytes via the LBK method has also been reported.¹²

The critical process variables for establishing polar order during APD of chromophoric polymers are not yet understood. Variables under investigation are (1) polymeric molecular structures, (2) solid substrate surface properties, (3) solution properties, (4) immersion processing conditions, (5) rinsing conditions, and (6) drying conditions. In most studies to date, the second-harmonic (SH) signal intensity, indicative of polar order, increased quadratically with the number of layers deposited only for the first 10–30 layers.^{5–8,13} Although the same amount of polymer continued to be deposited with each additional dipping cycle (as measured by a linear increase in UV–vis absorption), the polar order soon reached a limiting value. One exception was recently

(1) Decher, G.; Lvov, Y.; Schmitt, J. *Thin Solid Films* **1994**, *244*, 772.

(2) Tsukruk, V. V.; Bliznyuk, V. N.; Visser, D.; Campbell, A. L.; Bunning, T. J.; Adams, W. W. *Macromolecules* **1997**, *30*, 6615.

(3) Phuvanarthnuruks, V.; McCarthy, T. J. *Macromolecules* **1998**, *31*, 1906.

(4) *Polymers for Second-Order Nonlinear Optics*; Lindsay, G. A., Singer, K. D., Eds.; Advances in Chemistry Series 601; American Chemical Society: Washington, DC, 1995; 414–468.

(5) Lvov, Y.; Yamada, S.; Kunitake, T. *Thin Solid Films* **1997**, *300*, 107.

(6) Wang, X.; et al. *Macromol. Rapid Commun.* **1997**, *18*, 451; and Balasubramanian, S.; Wang, X.; Wang, H. C.; Yang, K.; Kumar, J.; Tripathy, S. K. *Chem. Mater.* **1998**, *10*, 1554.

(7) Figura, C.; Marciu, D.; Liu, Y.; Wang, Y. X.; Lenaham, K.; Claus, R. O.; Heflin, J. R. *ACS Polym. Prepr.* **1998**, *39* (2), 1126.

(8) Laschewsky, A.; Wischerhoff, E.; Kauranen, M.; Persoons, A. *Macromolecules* **1997**, *30*, 8304.

(9) Ulman, A. *Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly*; Academic Press: New York, 1991.

(10) Lin, W.; et al. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1497.

(11) Laschewsky, A.; et al., *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2788.

(12) Roberts, M. J.; et al. In *Organic Thin Films*; Frank, C. W., Ed.; ACS Symposium Series 695; American Chemical Society: Washington, DC, 1997; pp 267–286.

(13) Roberts, M. J.; et al. *Proc. SPIE* **1998**, *3281*, 126.

reported by Heflin et al., who observed a quadratic increase in SH intensity with the number of layers out to 100 bilayers.⁷

In all of the above APD NLO film studies, only one of the two polyelectrolytes employed was NLO-chromophoric, usually the anionic polymer. The other polymer was NLO-inactive and, of course, lowered the concentration of the chromophores in the bulk film. In the present study, both the anionic and cationic polymers were chromophoric and each contributed to the polar order.

Experimental Section

Materials and Characterization. All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) unless otherwise specified. Polymers were characterized by proton and carbon nuclear magnetic resonance (NMR), using Brücker spectrometers, and by differential scanning calorimetry (DSC), using a TA Instruments 2100 thermal analyzer.

Synthesis of Polymer 1 [Polyepichlorohydrin–Picolinium Chloride Adduct]. Four grams of poly(epichlorohydrin) (PECH; 50 mmol of chloromethyl groups) having a molecular weight of about 1000 g/mol (a sample from 3M, Corp., St. Paul, MN) was dissolved in 180 mmol of freshly distilled 4-picoline. The contents were refluxed at 150 °C overnight under a positive nitrogen blanket. Most of the unreacted picoline was removed by constant rotation under vacuum. The crude polymer was dried at room temperature in a vacuum overnight. The dried polymer was redissolved in methanol and extracted three times with cyclohexane. The methanolic phase was reduced to an oily residue, by constant rotation under vacuum, and then further dried at room-temperature overnight in a vacuum at 0.05 Torr. A brown solid (3.10 g) was obtained in 40% yield (polymer dissolved in cyclohexane phase was not recovered). Conversion of the chloromethyl groups to picolinium chloride was 98% by NMR. ¹H NMR (200 MHz, MeOH-*d*₄, ppm): δ 2.67 (s, 3H), 3.67–4.13 (m_{br}, 3H), 4.73 (m, 2H), 8.01 (m, 2H), and 8.9 (m, 2H).

Synthesis of Compound 2 [Ethyl *N*-Ethyl-*N*-(4-formylphenyl)glycine]. A mixture of ethylaniline (24.2 g, 0.20 mol), ethyl bromoacetate (33.4 g, 0.20 mol), and sodium bicarbonate (18 g, 0.215 mol) in 100 mL of dry DMF was heated at reflux for 72 h. The mixture was then cooled, poured into 1 L of water, and extracted with ether (2 × 100 mL). The combined extracts were washed with water (3 × 800 mL), dried (MgSO₄), and evaporated at reduced pressure, giving 21.0 g (51% yield) of a light brown oil, **2a**, which was used without further purification in the next step. ¹H NMR (200 MHz, CDCl₃, ppm) δ 7.22 (2H, m), 6.68 (3H, m), 4.16 (2H, q, *J* = 9 Hz), 4.02 (2H, s), 3.48 (2H, q, *J* = 9 Hz), 1.35–1.15 (6H, m of overlapping t's).

Then a solution of the above light brown oil **2a** (5.12 g, 0.025 mol) in 3 mL of 1,2-dichloroethane was added to a mixture of DMF (11.8 g, 0.162 mol) and POCl₃ (19.8 g, 0.13 mol) at about 70 °C with stirring (Vilsmeier's reaction). The temperature was then slowly raised to 85 °C over 2 h, then the mixture was cooled and poured into a mixture of 150 mL of chloroform/400 mL of water and stirred for 2 h. The chloroform layer was separated and the aqueous layer extracted with 100 mL of chloroform. The combined chloroform solutions were washed with water (4 × 150 mL), dried (MgSO₄), and evaporated at reduced pressure, giving 3.70 g (64% yield) of a yellow-brown oil, **2**, which was used without further purification in the next step. ¹H NMR (200 MHz, CDCl₃, ppm): δ 9.70 (1H, s), 7.15 (2H, d, *J* = 11 Hz), 6.60 (2H, d, *J* = 11 Hz), 4.15 (2H, q, *J* = 9 Hz), 4.02 (2H, s), 3.48 (2H, q, *J* = 9 Hz), 1.4–1.15 (6H, m of overlapping t's).

Synthesis of S-PECH. Polymer **1** (0.5 g, 1.0 mmol of picolinium groups) and compound **2** (0.63 g, 1.2 mmol) were dissolved in 5 mL of methanol, and piperidine (3 drops) was added as a catalyst to this mixture. The solution was degassed and refluxed in a stirred round-bottom flask for 2 days under

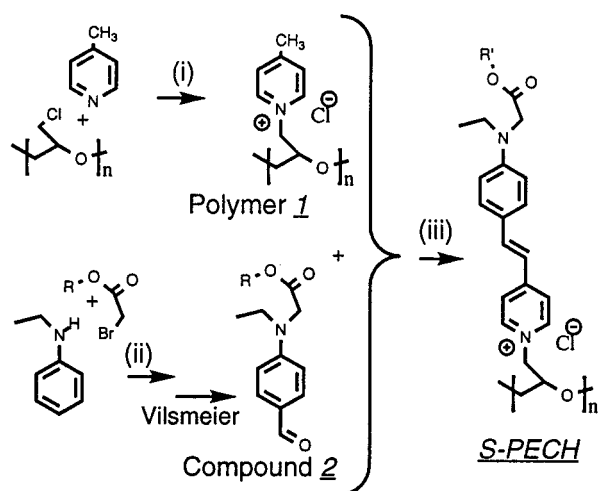


Figure 1. Preparation of the cationic NLO polymer, S-PECH; conditions for (i), (ii), and (iii) are given in the text. R = ethyl, and R' = methyl (after dialysis with methanol).

a positive nitrogen blanket. During this time the solvent evaporated and the temperature in the flask reached 90 °C. The solid residue was then redissolved in methanol and precipitated into a large excess of diethyl ether. The turbid ether was decanted from the oily solid residue, and this oily solid residue was dried in a vacuum overnight at 0.05 Torr at room temperature; whereupon, it became a black glass. (Similar polymers have been reported in our earlier papers involving fabrication of NLO films by Langmuir–Blodgett–Kuhn deposition.¹⁴) The polymer was redissolved in methanol and dialyzed with methanol for 3 days. The methanol was removed from the dialyzed polymer by evaporation with a continuous stream of dry nitrogen for 2 days to form a glassy, red-black polymer film (47% yield of S-PECH; the polymer that passed through the dialysis membrane was not recovered).

An essential question to answer for this study was whether the ethyl ester on the stilbazolium side chain was transesterified with methanol and/or hydrolyzed with adventitious water during dialysis. This question was answered using proton and carbon NMR: the spectroscopic evidence indicates that the pendant group is, in fact, the methyl ester. No free acid hydrolysis product was detected. The glass transition temperature (*T*_g) of the methyl ester polymer (after dialysis) was not measured, but it should be slightly higher than the *T*_g of the ethyl ester polymer (before dialysis), which was 163 °C. NMR analysis of the dialyzed polymer indicated that 98% of the picolinium groups were converted to stilbazolium chromophore groups.

Proton NMR Assignments of S-PECH in DMSO-*d*₆ after Dialysis in Methanol (Figure 2). The aromatic region of the spectrum is well-resolved and consistent with the proposed structure, as is the single methyl resonance assigned to the *N*-ethyl group. Note that there is only one proton resonance in the methyl region (ca. 1 ppm); one would expect two resonances in this region if an ethyl ester were present. Although the region of the spectrum between 3 and 5 ppm consists of a series of overlapping bands, from shift considerations, resonances in this region must arise from the methylene of the *N*-ethyl group, the methylenes bridging the nitrogen and carbonyl carbon, the polymer backbone, and the oxymethyl (and oxymethylene of residual ethyl ester, if present). We assign the resonance at 4.28 ppm to the methylene connecting the amine nitrogen and the carbonyl carbon and the resonance at 3.43 ppm to the methylene of the *N*-ethyl. The sharp resonance at 3.48 ppm may arise from methyl ester (and the methylene of residual ethyl ester if present).

(14) Hall, R. C.; Lindsay, G. A.; Anderson, B.; Kowel, S. T.; Higgins, B. G.; Stroeve, P. *Mater. Res. Soc. Symp. Proc.* **1989**, *109*, 351; and Hall, R. C.; Lindsay, G. A.; Hoover, J. M. U.S. Patent 5,162,453, 1992.

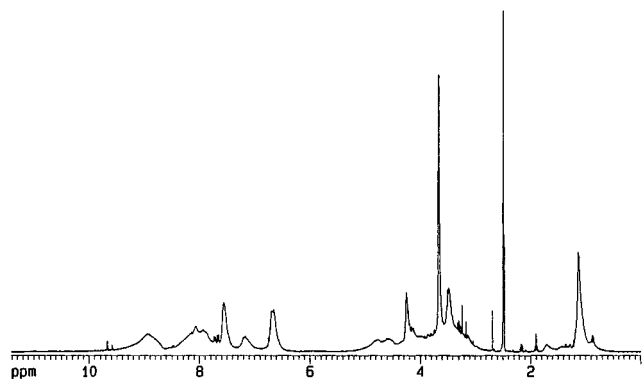


Figure 2. The proton NMR (in DMSO- d_6 solvent) of S-PECH after dialysis in methanol.

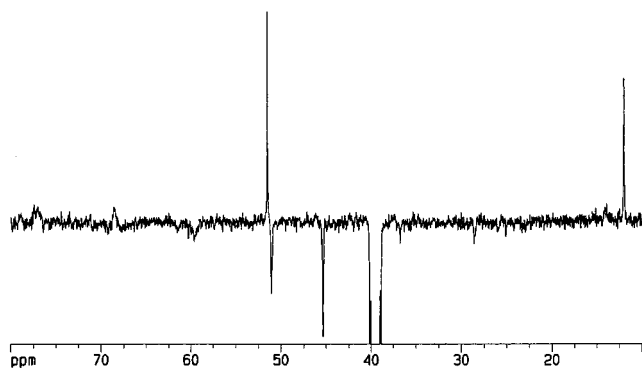


Figure 3. The carbon NMR (in DMSO- d_6 solvent) of S-PECH after dialysis in methanol. The Gated Spin-Echo (GASPE) NMR method was used [see LeCocq, C.; Lallemand, J. Y. *J. Chem. Soc., Chem. Commun.* **1981**, 150].

Because separate integration of these resonances was not possible, we chose to compare overall integration for the three major regions of the spectrum: 6–8 ppm (total aromatic), 3–5 ppm (described above), and 0.8–1.2 ppm (methyl of the *N*-ethyl). Integration of these regions for the three possible structures (assuming overlap of the methyl groups of the *N*-ethyl and ethyl ester) would result in (1) 10:12:3 for the methyl ester, (2) 10:11:6 for the ethyl ester, or (3) 10:9:3 for the carboxylic acid. The actual integration determined was 10:12.2:3.3, which strongly indicates the presence of only the methyl ester. One might argue that the integration of the 3–5 ppm region may be skewed by the presence of adventitious water; however, we do not believe this to be the case. Dry DMSO- d_6 from sealed ampules was used and the sample was made as concentrated as possible to reduce the relative amount of water in the sample. Further, the spectrum was compared with a spectrum of the same material before rigorous drying, which showed a clear water resonance at 3.26 ppm. No similar resonance is present in this spectrum (Figure 2).

Carbon NMR Assignments of S-PECH in DMSO- d_6 after Methanol Dialysis (Figure 3). Several aspects of the 10–80 ppm region support the absence of the ethyl ester and the presence of the methyl ester. In this experiment, quaternary and methylene carbons will phase down and methyl and methyne carbons will phase up. The very broad resonances of the PECH backbone can be seen in the 58–80 ppm region. This assignment has been confirmed by comparison to carbon spectra of the starting material and the picolinium-substituted PECH (Merwin and Zarras, unpublished results). There is only one resonance in the methyl group region at 10–15 ppm. In contrast, the methyl groups of the *N*-ethyl and ethyl ester substituents of the aldehyde starting compound **2** are clearly well-resolved at 14.6 and 12.6 ppm. The aromatic region is consistent with the proposed structure and will not be discussed further. One does not observe a sharp resonance in the ca. 60 ppm region, which could be assigned to the methylene of an ethyl ester. Again this is in contrast to compound **2**,

where the ethyl ester methylene carbon is found at 62.4 ppm. Evidence for the methyl ester is found in the sharp, upwardly pointing line at 51.5 ppm in Figure 3. From the experiment, this must either be a methyl or aliphatic methyne. As the backbone methyne and *N*-ethyl methyl have already been accounted for, and assignment to these would not be consistent with shift considerations, we assign this resonance to the methyl ester. The line width and position¹⁵ are consistent with this assignment. To complete the picture, the downward phased lines at 51.1 and 45.3 can be assigned to the bridging methylene and *N*-ethyl groups, respectively. A more complete NMR analysis of this and related polymers will be published elsewhere. In summary, the carbon and proton assignments noted are all consistent with the S-PECH being fully converted to the methyl ester.

Synthesis of Monomer 4. The synthesis was previously reported.¹⁶

The Synthesis of Monomer 5 [N,N-Biscarboethoxymethyl-N,N-diphenylethylenediamine]. (a) Synthesis of the Diester 5a. A mixture of *N,N*-diphenylethylenediamine (8.1 g, 0.034 mol, contaminated with 10% *N,N*-diphenylpiperazine), sodium bicarbonate (7 g, 0.083 mol), and ethyl bromoacetate (13.2 g, 0.079 mol) in 60 mL of dry DMF was heated at reflux for 24 h. After cooling, the mixture was poured over 150 g of ice and water. The precipitated gum solidified and was washed with water, filtered, air-dried, and recrystallized from 130 mL of absolute ethanol, giving off-white platelets (12.9 g), mp 70–80°. A second recrystallization from absolute ethanol gave white platelets, mp 85–88 °C. ¹H NMR (200 MHz, acetone- d_6 , ppm): δ 7.24–6.61 (10H, m, ArH), 4.15 (4H, s), 4.13 (4H, q, $J = 5$ Hz), 3.74 (4H, s), 1.23 (6H, t, $J = 5$ Hz).

Synthesis of 5 by the Vilsmeier Reaction of 5a. To a mixture of dry DMF (10 g, 0.137 mol) and POCl₃ (16.8 g, 0.109 mol) at 70 °C was added **5a** (4 g, 0.0104 mol) slowly with stirring. After the addition was complete, the mixture was then heated at 95 °C for 4 h. After cooling, the reaction was diluted with 50 mL of CHCl₃, which in turn was then added to a mixture of 250 mL of CHCl₃/400 mL of water and stirred for 30 min. The layers were separated, and the aqueous phase was re-extracted with CHCl₃ (2 \times 150 mL). The combined CHCl₃ extracts were washed with water (2 \times 100 mL), dried (MgSO₄), filtered, and evaporated at reduced pressure, giving a yellow solid (3.27 g, 71% yield), mp 153–9 °C. A small sample was recrystallized from ethanol, yielding fine yellow crystals, mp 161.5–2.5 °C. ¹H NMR (200 MHz, acetone- d_6 , ppm) δ 9.76 (2H, s), 7.77–6.82 (8H, m-AA'BB'), 4.37 (4H, s), 4.18 (4H, q, $J = 7$ Hz), 3.95 (4H, s), 1.23 (6H, t, $J = 7$ Hz).

Synthesis of C-ACCORD [the Sodium Salt of Poly(2-((4-(2-(*N*-2-hydroxyethyl)carbamoyl)-2-cyanovinyl)phenyl)(2-((4-(2-(*N*-methylcarbamoyl)-2-cyanovinyl)phenyl)(carboxymethyl)amino)ethyl)amino)acetic Acid)]. A mixture of monomers **4** (0.1245 g, 0.28 mmol) and **5** (0.0633 g, 0.28 mmol) and 4-(dimethylamino)pyridine (0.1 g, 0.9 mmol) were dissolved in 15 mL of pyridine and heated to 120 °C. After 5 days, the average degree of polymerization was estimated to be approximately 15 units (30 chromophores) from the number of aldehyde end groups (¹H NMR analysis). The solution was then cooled, precipitated into absolute ethanol, stirred overnight, filtered, and dried to give about 0.28 g of wet polymer. The T_g of the ethyl ester polymer (before converting it to the sodium salt) was 188 °C. ¹H NMR (200 MHz; DMSO- d_6 , ppm): δ 8.1 (1H, s), 7.9 (2H, d), 7.4 (1H, m), 6.8 (2H, d), 4.4 (1H, s), 4.2 (2H, q), 3.8 (2H, s), 3.3 (4H, m), 1.1 (3H, t).

Conversion of this polymer's ester groups to the carboxylate sodium salt was done by suspending 0.13 g of wet polymer in 10 mL of 1.0 N NaOH and stirring the mixture overnight. The solution became completely homogeneous. The solution was

(15) Kalinowski, H.; Berger, S.; Braun, S. Chapter 3. *Carbon-13 NMR Spectroscopy*; John Wiley & Sons: New York, NY, 1988.

(16) Lindsay, G. A.; Stenger-Smith, J. D.; Henry, R. A.; Hoover, J. M.; Nissan, R. A.; Wynne, K. J. *Macromolecules* **1992**, 25 (22), 6075.

dialyzed with 500 molecular weight cutoff dialysis tubing against deionized water and then finally against 18 M Ω cm resistivity water to remove the low molecular weight compounds.

Preparation of Solutions. All polymer solutions were made from water taken from a Barnstead Nanopure purification system (17.9 M Ω cm resistivity, 0.2 μ m filter). The solutions were diluted by pipet to the concentration range of 10^{-4} – 10^{-7} moles of ionic repeat units per liter. After dilution, all polymer solutions were filtered through 0.5- μ m membrane Millipore filters directly into the dipping vessels. By adding a few drops of 0.1 N NaOH, C-ACCORD solutions were adjusted to a pH of 8.0, and S-PECH solutions were adjusted to a pH of between 8 and 10. At this pH, although slow hydrolysis of the stilbazole is possible, there was no evidence of hydrolysis: the color and absorption intensity of the S-PECH solutions remained constant for over 20 h. At no time were other salts added. Poly(sodium 4-styrenesulfonate), PSS, having a weight-average molecular weight of 70 000 (sold by Aldrich) was used to make a 10^{-4} M solution by diluting the as-received 20 wt % water solution with ultrapure water. Solutions were stored in the dark not more than a few hours at approximately 23 °C before adding to the dipping vessels. The dipping vessels were either 50 cm³ glass beakers or plastic baths used in a Zeiss HMS programmable slide stainer (Carl Zeiss, Thornwood, NY).

Preparation of Substrates. The substrates were glass microscope slides from Fisher (Cat. # 12-550A). They were cleaned with H₂SO₄/H₂O₂/H₂O (7:1:2) for 5 min and dried at 100 °C for 1 h. [CAUTION: this is a highly corrosive acid and must be handled with extreme care.] Cleaned slides were made hydrophobic by exposure to neat, refluxing hexamethyldisilazane for about 1 h. The surface energy of the hydrophobic glass slides was characterized by contact-angle measurements. A contact angle of 90° is typical for complete trimethyl silyl coverage of glass. The contact angle of these substrates was about 64° (about as hydrophobic as pyrolytic carbon),¹⁷ which indicates slightly less than complete trimethyl silyl coverage. The glass slides were then either immediately used or stored over anhydrous CaSO₄ under vacuum.

Deposition of Multilayers. The solutions were kept in the dark at room temperature (approximately 23 °C) during the film depositions. Depositions were performed in a Class 100 clean room under filtered fluorescent lighting. For the deposition of S-PECH, the hydrophobic glass slide was immersed in the polycation solution for 60 min, which was just long enough to develop the maximum SH intensity of the first S-PECH layer on trimethylsilylated glass. The slide was rinsed three times in ultrapure water for 10 s. The slide was dried for 5 min in air before the next immersion step. For the deposition of C-ACCORD, the glass slide containing a dry S-PECH polymer layer on the surface was immersed in the polyanion solution for 20 min. The slide was removed, rinsed in ultrapure water three times for 10 s, and dried for 10 min. Films of the inert PSS (used in place of C-ACCORD) were deposited by the same procedure, except a 10^{-4} M solution was used. Subsequent bilayers were built up on the substrate by alternating between the polycation and polyanion solutions with the same rinsing and drying steps after each deposition.

It was noted that after the polymer solutions aged overnight, the observed UV–vis absorption of the film ceased to increase linearly as more layers were deposited (even though the UV–vis absorption of the dipping solution appeared unchanged). To remedy this situation, fresh polymer solutions were prepared and used after approximately every eight bilayers of deposition. When this procedure was followed, uniform layer-by-layer deposition was again observed.

Characterization of the APD Films. The spectra of the films in transmission were obtained with a Cary 5 UV–vis–NIR spectrometer. The films were referenced to glass, and the

glass background was subtracted to obtain the film spectra. SH generation measurements were made in transmission with the incident beam at approximately 54° from normal to the film. The SH signal was generated by transmission of a fundamental beam from a Q-switched Nd:YAG laser operating at 1064 nm, with a pulse width of 10 ns and repetition rate of 10 Hz. The SH signal was detected with an intensified Tracor Northern Si diode array, and each data point was an average of 1500 pulses. The films were featureless, highly uniform, and transparent. No liquid crystal textures were observed by polarized microscopy.

Results

Deposition. A “layer” is defined as the amount of polyelectrolyte deposited on a solid substrate in one immersion step, and a “bilayer” is defined as the amount of poly(cationomer) and poly(anionomer) deposited in two consecutive immersion steps. Interactions between the polymer in solution and the substrate surface undoubtedly play a major role in determining layer thickness. Unlike a layer deposited by the LBK method, the thickness of a freshly deposited APD layer may depend to some extent on the ionic strength of the dipping solution. For example, it has been shown that layer thickness can increase with the increasing ionic strength of the polyelectrolyte solution.¹⁸ This increase in thickness is likely due to trapped loops of polymer sticking up from the surface. Therefore, dilute polymer solutions with no additional salts were used in this study, in order to minimize trapped loops of polymer, which would cause uncompensated charges in the bilayer.

The initial dipping strategy was to deposit a monolayer of polydiallyldimethylammonium chloride (PDDA) on base-washed glass and use this as the substrate for laying down the first layer of C-ACCORD. However, no second-harmonic signal was observed after depositing the first layer of C-ACCORD, so this approach was abandoned.

A more successful approach started with a hydrophobic glass substrate. Upon immersing it in an aqueous solution of S-PECH for about 50 min, a strong SH signal was observed with the very first layer. It is interesting to note that although deposition of the S-PECH layer was complete in less than 15 min (as determined by the increase and then saturation in UV–visible absorbance), it took nearly 1 h to develop the maximum intensity of the SH signal.

This dipping strategy was continued for 20 bilayers (Figure 5). The absorption correction on the SH intensity was neglected, because the films are so thin. The amount of polymer deposited with each dipping cycle was essentially constant, as seen by the linear increase in UV–visible absorption as a function of the number of bilayers. If the same degree of polar order were obtained for each deposition cycle, one would expect to see a quadratic increase in the second harmonic as a function of the number of bilayers. This is observed for the first 10 bilayers; however, beyond that number, it appears that polar order in subsequent layers is absent. Furthermore, one would have expected to see an in-

(17) Adamson, A. *Physical Chemistry of Surfaces*, 5th ed.; John Wiley: New York, p 397.

(18) Clark, S. L.; Montague, M. F.; Hammond, P. T. *Macromolecules* 1997, 30, 7237.

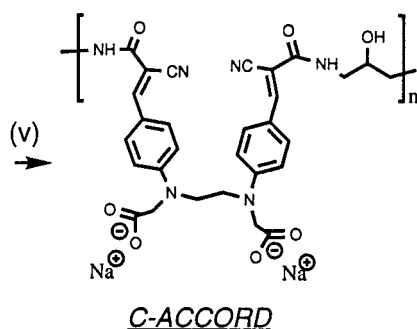
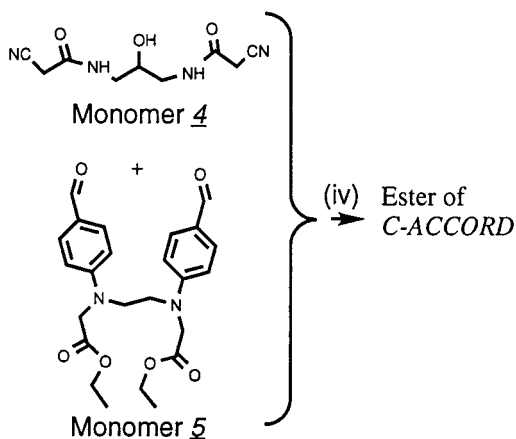


Figure 4. Preparation of the anionic NLO accordion polymer,¹⁶ C-ACCORD. Conditions for (iv) and (v) are given in the text.

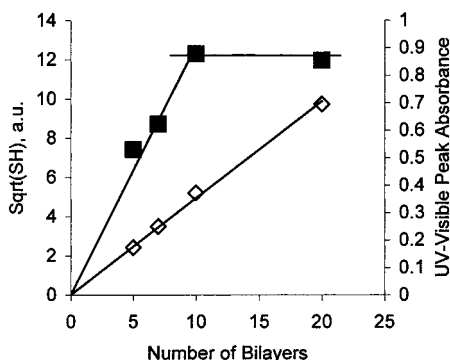


Figure 5. Square symbols are the SH intensity and diamonds are UV-visible intensity after deposition of up to 20 C-ACCORD/S-PECH bilayers.

crease in absorption per layer after 10 bilayers, due to a decrease in polar orientation. This not being the case may indicate that the polar order parameter of the first 10 bilayers is small. The d_{33} is estimated to be about eight times that of quartz.¹⁹

Using an Inert Interlayer Polymer (Figure 6). To compare the effect of using an NLO-*inactive* polyelectrolyte with the above results, PSS was substituted for C-ACCORD. As in the previous case, the first layer deposited was S-PECH on hydrophobic glass. As shown in Figure 6, the square root of the SH intensity was decreased per bilayer when PSS was substituted for C-ACCORD. The deposition conditions (see Experimental Section) were very similar for these two films.

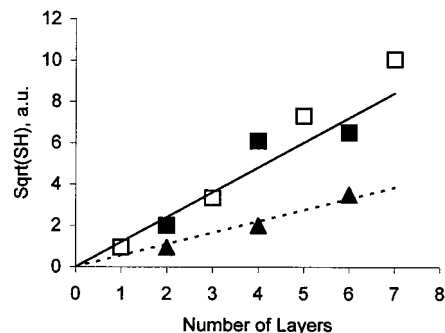


Figure 6. The open squares show SH intensity after the deposition of the cationic S-PECH layer. The solid triangles show the SH intensity after deposition of the inert PSS and solid squares, after deposition of C-ACCORD.

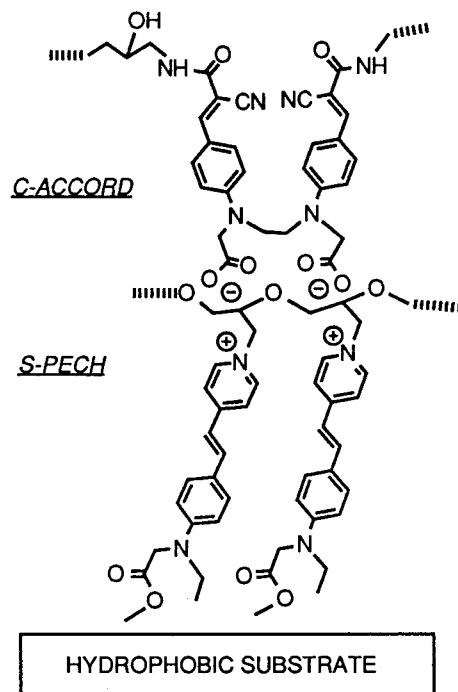


Figure 7. Ionically bound bilayer of S-PECH and C-ACCORD.

Discussion

Motivation. This is the first report on alternating polyelectrolyte deposition (APD) in which both anionic and cationic polymers were NLO-active. The motivation for this is to double the NLO properties for a given film thickness. The side chain stilbazolium polymer, S-PECH, was chosen for this study because the cationic charge was located near the backbone. Hence, the force due to charge repulsion at the ends of the chromophore is countered by the constraint of the backbone. The syndioregic main chain chromophoric polymer, C-ACCORD, was chosen because the spatial location of charges on C-ACCORD lies in close register with those on S-PECH in the polar conformation (see Figure 7), and this novel backbone configuration of chromophores had not yet been investigated for APD.

Formation of Polar Order. Initially, it was found that when a cationic substrate (polydiallyldimethylammonium chloride on glass) was dipped in a solution of the anionic C-ACCORD, essentially no polar order was observed. The reason for this was not clear. So a new strategy was employed. Upon dipping the initial hydro-

(19) Roberts, M. J.; Lindsay, G. A.; Herman, W. N.; Wynne, K. J. *J. Am. Chem. Soc.* **1998**, *120*, 11202.

phobic substrate in the cationic S-PECH solution, strong polar order was observed, but only after about 50 min. The UV-vis absorption indicated that the polymer film was fully formed on the substrate in less than 10 min. Hence, the initial conformation of the absorbed S-PECH is in a nonpolar and metastable state. Initially, the chromophores may be lying relatively flat on the surface to minimize contact between water and the hydrophobic substrate. As more polymer becomes available by diffusion to the surface, the relatively hydrophobic ends of the chromophores stay near the surface and the cationic charges move toward the aqueous medium, creating a net polar orientation. Increasing the temperature accelerates this process (to be published elsewhere).

To continue having the polar order in each of the subsequent layers, a number of synergistic architectural features appear to be important. In forming layer 2, of great importance is the attraction between the cations at the surface of layer 1 and the anions in C-ACCORD. This attraction is driven thermodynamically by the formation of the polymer-polymer salt bilayer with the concomitant release of the Na^+ and Cl^- mobile ions into the aqueous phase. The design of C-ACCORD, with the anionic sites adjacent to the electron donor end of the chromophore, is essential for the molecular hyperpolarizability of layer 2 to reinforce that of layer 1. Furthermore, in the folded (accordion) conformation, the anionic sites in C-ACCORD are spatially commensurate with the corresponding cationic charges in layer 1. As seen in Figure 7, this provides an enhanced driving force for the formation of the folded chain conformation (which otherwise may have been energetically unfavorable relative to a more extended conformation). Finally, the formation of a fully charge-compensated salt bilayer favors the placement of the nonionic hydroxyl functional end of C-ACCORD chromophores at the surface of layer 2 setting the stage for the adsorption of layer 3.

To explain the continuing polar alignment of the third layer, it is presumed that S-PECH from the solution phase, as it absorbs, forms hydrogen bonds between its carbonyl groups and the hydroxyl groups of layer 2. In this way it would present its cationic charges toward the aqueous medium with its nonionic head buried against the C-ACCORD layer. It would be surprising that layer-by-layer formation of polar alignment could occur if the negative charges in the C-ACCORD layer 2 had not been nearly completely compensated by the charges in the S-PECH layer 1. Even if a few anionic charges did remain uncompensated in the second layer,

apparently the hydrogen bonding and hydrophobic-hydrophobic interactions win out, and the third layer exhibits polar order.

For layer 4, the process postulated for layer 2 would be repeated. If polar order begins to wane, it would likely be due to an accumulation of uncompensated charges and other defects.

Retention of Polar Order. It is remarkable that these films retain polar order during the dipping process. The films are immersed with ample time to become saturated with water. While under water, the T_g of these layers is likely to be near or below room temperature, giving the polar order ample time to relax. The fact that polar order is retained is most likely due to interlayer cross-linking by the plurality of ionic bonds between bilayers in the solid-state preventing rotational diffusion of the chromophores, even when submerged in water.

When the films are dried, the glass transition temperature should most likely lie at least between the T_g s of the starting dry S-PECH and C-ACCORD (165 and 185 °C, respectively). Hence, the long-term stability of these films is expected to be quite good up to 85 °C.¹⁹

Conclusions

The APD process is a promising new method for the fabrication of second-order nonlinear optical films. However, there is much yet to be learned about making thick polar films by the APD process (the polar order was maintained in this study for only the first 20 chromophoric layers). In this study, in which both the anionic and cationic polyelectrolytes contributed to the NLO activity of the multilayer film, the strategy used was to optimize conditions for the complete compensation of charges at one interface. That is, at the center of the bilayer, one polymer compensates the charges in the other polymer. The other interface is more hydrophobic (the one between two charge-compensated bilayers) and is presumably held together by means of specific hydrogen bonds between the two polymers. For other polymer systems, there may be completely different dipping strategies that also give polar order. This exciting field obviously needs further investigation.

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