11202 *J. Am. Chem. Soc.* **1998,** *120,* 11202−11203

Thermally Stable Nonlinear Optical Films by Alternating Polyelectrolyte Deposition on Hydrophobic Substrates

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Received June 29, 1998

Alternating polyelectrolyte deposition (APD) is a layer-by-layer technique for the formation of polymer films.[1] Film deposition is achieved by alternately immersing a substrate in aqueous solutions of a polyanion and a polycation. The thickness of each layer can be as low as 1.0 nm.[2] Therefore, APD allows precise control of the overall film thickness that through automated processing may exceed a thousand layers.

Coulombic forces are largely responsible for the formation of APD films. Although the strength of each individual ionic bond is weak compared to covalent bonds, the resulting structure is robust because of the large density of ionic bonds. APD has been used to produce films of materials such as electrically conducting polymers,[3] conjugated polymers for light emitting diodes (LED),[4] proteins,[5] and nanoparticles.[6] Acentric APD films of second-order nonlinear optical polymers (NLOPs) have also been reported.[7]

The fundamental mechanism that causes noncentrosymmetric chromophore orientation in multilayer APD NLO films remains unproven, but a number of research groups have confirmed that polar films are obtained.[8−10] One group has recently reported second-harmonic generated (SHG) light intensity increasing quadratically with film thickness over one hundred bilayers, although $\chi^{(2)}$ values were modest and comparable to those for quartz.[11] We communicate here the remarkable thermal stability of acentric APD films of stilbazolium-substituted polyepichlorohydrin (SPECH) and poly(sodium 4-styrenesulfonate) (PSS) (Figure 1).

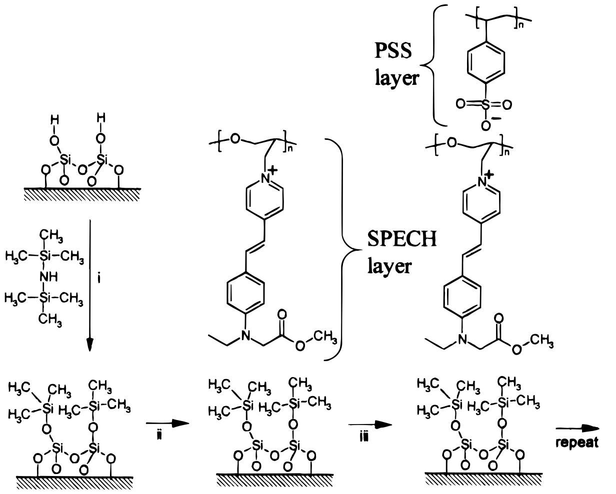

Figure 1. Formation of multilayers of SPECH and PSS by APD on HMDS-treated glass: (i) glass cleaned in piranha solution is exposed to refluxing HMDS, (ii) substrate is dried and immersed in SPECH aqueous solution for 50 min, (iii) substrate is rinsed and then immersed in PSS aqueous solution for 20 min. The substrate with SPECH/PSS bilayer(s) is rinsed and dried before repeating from step ii. Note that the tilt angle of the chromophore has not been determined experimentally.

The synthesis and characterization of SPECH will be reported elsewhere, but the procedure is similar to that found in a previous report.[12] The glass transition temperature (T_g) of bulk SPECH is 165 °C and its average number of repeat units is 10 with 95% chromophore substitution (determined by ^{1}H NMR). The T_g of PSS (Aldrich, Milwaukee, WI) has not been measured, but the thermal decomposition temperature is 300 °C, and its weight average molecular weight is approximately 70 000 g/mol. Solutions were prepared with ultrapure water (18 MΩ·cm) from a Barnstead Nanopure water purification system. The SPECH solution was 10^{-6} M. The PSS solution was 2×10^{-4} M (0.04 mg/mL), made by diluting a 20 wt % water solution.

The hydrophobic substrates were glass slides (Fisher, Cat. No. 12-550A) cleaned with $H_2SO_4/H_2O_2/H_2O$ (7:1:2) for 20 min, dried at 100 °C for 1 h, and made hydrophobic by exposure to refluxing hexamethyldisilazane (Aldrich) for 30 min. The effects of substrate preparation variables on multilayer APD will be reported elsewhere. The polymer solutions were filtered through Millipore 0.5-μm pore-size membrane filters. The polymer solutions had a pH of 5.5 and no salts were added. Films were deposited at room temperature (approximately 23 °C) by using a computer-interfaced Zeiss HMS Programmable Slide Stainer (Carl Zeiss, Thornwood, NY) that was kept in a Class 100 clean room under filtered fluorescent lighting (UV through the blue end of the spectrum blocked) and ambient air.

To deposit multilayer films, hydrophobic glass slides were immersed in SPECH solution for 50 min, rinsed three times in ultrapure water for 10 s, immersed in PSS solution for 20 min, rinsed three times in ultrapure water for 10 s, and then dried for 30 min. Subsequent bilayers were built up on the substrate by repeating the deposition procedure. The polymer solutions were replaced with new solutions after approximately every 8 bilayers of deposition because the amount of SPECH adsorbed per deposition cycle was observed to decrease if the solution was

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Published on Web 10/16/1998

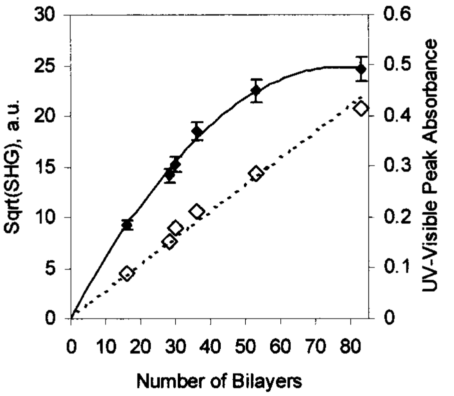

Figure 2. SHG intensity (filled diamonds) and peak maximum UV−visible absorbance (open diamonds) plotted as a function of the number of deposited bilayers of SPECH and PSS on hydrophobic glass. Each point represents data from separately deposited films.

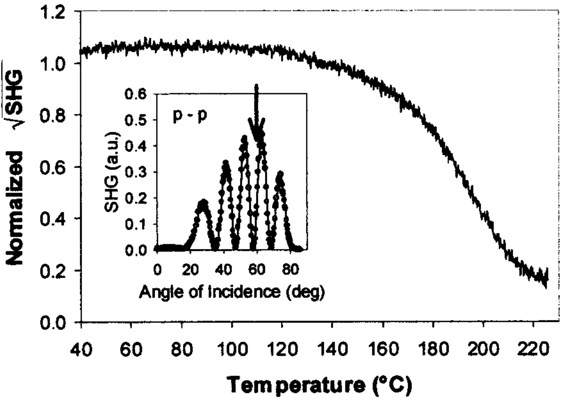

Figure 3. Temperature stability of SHG intensity is plotted for a 30-bilayer APD film of SPECH and PSS. The inset shows the interference of the Maker fringes from the two sides of a substrate coated with APD films on both sides. The arrow indicates the angle of incidence at which SHG data were taken as the temperature was increased.

not refreshed. Methods of film characterization by UV−visible spectroscopy and transmission SHG measurements have been described previously.[10]

The peak maximum UV−visible absorbance in transmission through the films is linear as a function of the number of bilayers (Figure 2). The SHG shows the expected quadratic increase up to 36 bilayers but then begins to level off and does not increase significantly above the value obtained for the 53-bilayer film. Thus, bilayers continue to be deposited, but the degree of polar order is decreasing within each new layer deposited beyond 36 bilayers. The reason that the SHG data begin to plateau is not understood at present.

For Maker fringe, azimuthal angle, and thermal stability the following procedure was used for measuring SHG. The sample was positioned at the waist of a focused (150 mm lens) fundamental beam (1319 nm) produced by a diode-pumped Q-switched Nd:YAG laser. The pulse width was 14 ns and the repetition rate 1 kHz. The fundamental beam was polarized inside the laser cavity and a half-wave plate was used to control the polarization of the beam incident on the sample. The second-harmonic signal was detected by a Hamamatsu R928 photomultiplier tube in conjunction with a Stanford Research SR250 boxcar averager, which was operated with active baseline subtraction. To account for laser power fluctuations, part of the fundamental beam was split off and sent through a lithium iodate crystal to produce a reference second harmonic signal. The sample was mounted on a computer-controlled Oriel rotation stage and a computer collected data. Thermal studies were performed with use of a computer-controlled oven to ramp the temperature at 1 deg C/min in air.

Figure 3 shows that 30-bilayer APD films of SPECH and PSS on both sides of hydrophobic glass retained 90% of the polar order up to 150 °C during a slow-temperature ramp of 1 deg C/min. The Maker fringes (Figure 3, inset) exhibit additional minima due to interference of the second harmonic generated at the two sides of the substrate that supports films on both sides. The fact that these minima go to zero indicates high-quality films. Azimuthal scans performed at 2 deg increments indicate that the polar order is isotropic in the plane described by the point group ∞_{mm} (data not shown). The $\chi^{(2)}$ values obtained were 3 to 4 times the value for quartz at a wavelength of 1.3 μm.

In this work, the formation on hydrophobic glass of acentric APD films with high thermal stability was demonstrated. The high thermal stability of the polar order makes the APD films potentially attractive for device applications. The thermal stability rivals that of the latest poled films.[13] There are several properties that remain to be measured to determine the usefulness of the polar APD films in electrooptical devices. The ionic conductivity in APD films will depend on the amount of residual mobile ions left in the film, but since a stable LED device made from APD films has been demonstrated,[4] there is room for optimism. The major challenge is to continue the polar ordering of the chromophores beyond a few dozen bilayers. Further characterization of the APD films by such surface analytical techniques as Kelvin probe microscopy may help locate the source of the disorder. The conditions of the film deposition (polymer concentration, length of immersion, effect of drying, etc.) continue to be explored systematically. The degree of polar order (electrooptic coefficient) will be measured in a future study.

Acknowledgment. The authors thank R. A. Hollins and P. Zarras for synthesizing the sample of SPECH and A. P. Chafin, R. Y. Yee, and J. D. Stenger-Smith for useful discussions. M.J.R. thanks M. D. Seltzer for the use of his laser equipment and D. Howie of Dr. M. Rubner's research group at MIT for the copy of his PC program, HMSPROXB, which interfaces the Zeiss Programmable Slide Stainer with a PC computer. W.N.H. thanks A. Samouris for assistance in thermal calibration. The ONR Division of Physical Sciences is acknowledged for funding this work.

JA9822613

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