# Solid-State Electrochromic Devices via Ionic Self-Assembled Multilayers (ISAM) of a Polyviologen[a]

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A PV was synthesized by polymerization of N,N'-bis(δ-aminopropyl)-4,4'-bipyridinium bromide hydrobromide (APD) and isophthaloyl chloride (ISP). The PV was completely soluble in water as well as in organic solvents. The spectroelectrochemical and EC properties of the resulting ionic self-assembled multilayers of PV/poly-(2-acrylamido-2-methylpropanesulfonic acid) (PAMPs) were examined by cyclic voltammetry, FT-IR spectroscopy, UV-vis spectroscopy, optical switching and current density measurements. Solid state devices made of PV films sandwiched with PANI as a counter electrode have switching times of 100–250 ms. 40 Bilayer films of PV/PAMPs show high contrast ($\Delta T = 61\%$) in 0.1 M $NaClO_4$ liquid electrolyte solution and CE as high as 57 $cm^2 \cdot C^{-1}$, one of the highest reported so far for any bipyridinium salt system.
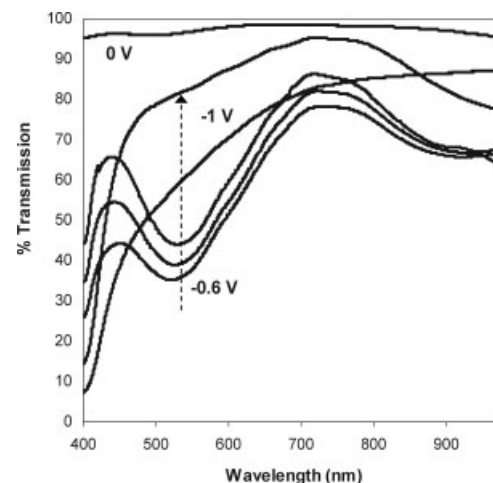
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Introduction

Electrochromic (EC) devices undergo reversible absorbance/transmittance change on application of external voltage.[1] Since the first major report on electrochromism, there has been much work done in the field of inorganic[2] and phthalocyanine[3,4] compounds as possible electrochromic materials, while the work with conducting polymeric[5,6] EC devices has gained significant attention in last decade or so. Other EC materials have been studied, but polyviologens (PV), which are bipyridinium systems, and their derivatives, have been widely investigated for more than 35 years because of their electrical and electrochromic properties and good environmental stability.[7] A great amount of work has been done for dialkyl bipyridinium

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units, but significant efforts have also been made from time to time on the modification of their chemical structures to improve the electrochromic properties[8] and film-forming abilities. Bipyridinium salts exhibit three redox states: the colorless dication (+2), colored radical cation (+1) and neutral. Out of all these states, the colorless dication is the most stable, followed by the radical cation, whose stability depends upon the delocalization of the radical electron in the π-framework. Electrochromism in bipyridinium species occurs due to the interconverison of these three species. Manipulation of the substituents at N and N′ modifies the color by attaining the appropriate molecular orbital energy levels. Suitable substitution not only results in "fine color tuning" of the PV system, but also results in the alteration of the redox and other physical properties without disturbing the electroactivity. Attached groups (aryl or alkyl) influence the reduction potential (E°), but further substitution of the aromatic system helps in tuning the rate of electron transfer between the redox species and influences the contrast, switching speed and coloration efficiency. Recently PVs have been applied in liquid crystal devices,[9] light emitting diodes,[10] printing[11] and frozen food monitoring.

The most common techniques to deposit EC polymers on electrodes are spin coating, thermal evaporation, surface polymerization by chemical means and electropolymerization, but the ionic self-assembled multilayer (ISAM) film fabrication method gives a fine degree of control to optimize the capabilities of EC films.[12,13] The unlimited thickness and robustness of the films with only nano-level roughness gives ISAM films advantages over conventional EC film fabrication methods. This technique developed by Decher et al.[14,15] uses the attractive forces between molecules of opposite charge to form the films. Several groups have studied the electrochromic properties of PV ISAM films.[6,7,16] The main reasons these systems are not used in displays are their slow-switching speeds and inability to work in solid-state form. Lee et al.[17,18] have studied the EC properties of polythiophene and poly-carbazole derivatives with a viologen as a pendant unit by electropolymerization, but the whole process was tedious and expensive and there is no report of the device stability, which has been one of the main drawbacks of PV-based EC devices.

Several groups have previously reported[19–22] PV EC devices on mesoporous electrodes for display purposes, but the major breakthrough in this field came from the work done by Ntera Inc.[23] Continuing towards the same aim, our group has assembled and fabricated fast-switching solid-state devices of PV with very high coloration efficiency, high contrast and long life, making them viable candidates for active-matrix displays. In this work, we report the synthesis of a PV[24] and its electro-chromic properties in ISAM films with poly(2-acrylamido-

2-methylpropanesulfonic acid) (PAMPs). Sammells et al.[25] incorporated PAMPs (10 wt.-% in water) within a heptylviologen system by suspending the latter with simple mixing; this brings higher contrast into the system with long-term write-erase efficiency but slows the response time to a significant extent. To improve the contrast in the system we preferred PAMPs at a very low weight percentage [4.125×10^{-2} wt.-% (2×10^{-3} M) in water] as a polyanion in the ISAM film assembly because of its natural ability to transfer ions, and the fact that it provides less bulk resistance and faster color change. The bilayers were characterized by cyclic voltammetry (CV), Fourier transform infrared (FT-IR) spectroscopy, UV-vis spectroscopy and current density and coloration efficiency (CE) measurements. In this study, we measured the electrochromic response of PV films in liquid electrolyte as well as solid state devices composed of PV/PAMPs slides sandwiched with film of polyaniline (PANI)/PAMPs.

Experimental Part

Materials

3-Bromopropylamine hydrobromide, Aldrich, 98%; 4,4′-bipyridyl, Aldrich, 98%, recrystallized from ethanol; isophthaloyl dichloride (ISP), Aldrich, 98%, recrystallized from petroleum ether and dried in vacuum; PAMPs, Aldrich; polyaniline in emeraldine base form, Aldrich; N,N-dimethylformamide, methylene chloride, pyridine and methanol, dried over 4 Å molecular sieves; tetrahydrofuran, dried over sodium/benzophenone; anhydrous ethanol, chloroben-zene, toluene, hexane, acetone, ethyl acetate, chloroform and dichloroethane, used as received. Sodium carbonate, magnesium sulfate, anhydrous sodium sulfate, calcium chloride, anhydrous potassium carbonate, NaOH and concentrated HCl, used as received.

Equipment

^{1}H and ^{13}C NMR spectra were acquired on a VARIAN 400 MHz spectrometer, with $CDCl_3/D_2O$ as the solvent, and chemical shifts (δ) are given relative to tetramethylsilane as the internal standard. Mass spectra were obtained on a Fisons VG Quattro instrument. The melting point was obtained on a Mel-temp II instrument. An EG & G 273 A potentiostat/galvanostat was used for CV studies. For electrochemical characterization, an indium tin oxide (ITO) coated glass slide was used as a working electrode, a Pt wire as the counter electrode, and a standard calomel electrode (SCE) as the reference electrode. Potential step chrono-amperometry was performed using a Voltalab 40 (Radiometer Analytical) instrument. An automated dipping machine from Nanostrata Inc. was used for deposition of the multilayer films. ITO-glass substrates with dimensions $3'' \times 1''$ were bought from Delta technologies. SEM images of the coated surface were taken on a LEO 1550 field emission scanning electron microscope (FESEM) at an accelerating voltage of 5 kV. Film thickness measurements were performed using a J. A. Woollam VB-2000 ellipsometer.

Film Fabrication

ISAM film fabrication was performed with the help of an automated slide stainer. The ITO slides were washed with water to develop some negative charge and then exposed to PV (pH 4, 2×10^{-3} M) solution for 6 min, followed by 3 steps of rigorous rinsing with de-ionized water for 45 s. Finally, the substrates were exposed to PAMPs (pH 4, 2×10^{-3} M) solution for 6 min and again rinsed with water for 45 s each in three consecutive water baths. This cycle was repeated 40 times to get the desired number of bilayers. The pH of the solutions was adjusted with sodium hydroxide or hydrochloric acid.

For solid state devices, as shown in the Figure 1, the PV/PAMPs multilayer film described above was sandwiched with another film with a few drops of PAMPs gel placed in between. The other film was fabricated as above with PANI instead of PV. The PAMPs component of these films is not electrochromic. It was found that a PV/PAMPs-PV/PAMPs sandwich did not have any color change with applied voltage, while the PV/PAMPs-PANI/PAMPs sandwich showed the same color change with an absorption peak at ≈515 nm as the PV/PAMPs in liquid electrolyte solution. This is distinguishable from the electrochromism of devices consisting of two PANI/PAMPs films, which we have shown in previous work to exhibit a peak absorption at 500 nm.[26]

Results and Discussion

The synthetic route for the bipyridinium monomer APD is shown in Scheme 1. The polymerization is shown in Scheme 2. A detailed explanation of the synthesis and IR, ^{1}H and ^{13}C NMR spectra is given in the Supplementary Information.

Film Thickness

Figure 2 shows the cross sectional view of the 40 bilayer film of PV/PAMPs; with little surface roughness, the thickness of the film varies between 190–210 nm. The total film thickness increases linearly with the number of bilayers according to the equation $t = 4.537b$ (Figure 3), where t is the total film thickness in nm and b is the number of bilayers. The overall variation in the actual film thickness from the reported values is ±2% of the total film thickness. The linear increase in the thickness by almost 4.5 nm per layer pair is true for the first few bilayers as well
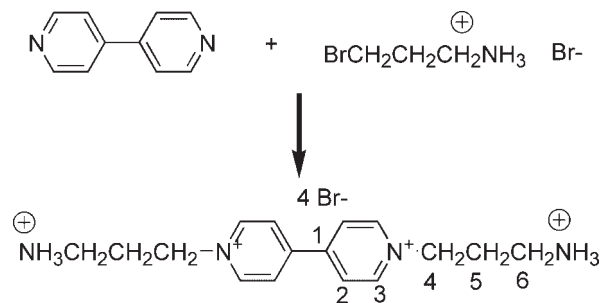
■ *Scheme 1.* Synthesis of APD.

as for higher numbers of bilayers. The film thicknesses were confirmed by ellipsometry.

The thickness of ISAM films formed by several other groups[7,13] did not increase in a linear fashion; one of the possible sources for that phenomenon is the relative concentration of the polyanion and polycation solutions. If the polyanion concentration is higher than the PV concentration, the films develop a globular morphology and increased roughness, which results in a super-linear or exponential increase in the film thickness with the number of bilayers. In our study, special care was taken to keep the same concentration (2×10^{-3} M) for both the PV and PAMPs solutions. Atomic force microscopy (AFM) images (not shown here) also confirm the extremely smooth and homogenous films of root mean square (RMS) surface roughness (Rq) of less than 2 nm for films with as many as 100 bilayers.

Coloration Efficiency (CE, η)

For the EC devices, the color change is better expressed in terms of coloration efficiency (η), which is determined at the wavelength maximum λ_{max}; in other words η is defined as the relationship between the changes in optical density to the total injected/ejected charge as a function of the electrode area.[27] For EC materials to be employed in fast-switching and efficient display operations, the value of η should be as high as possible. There has been a report of η as high as 1 400 cm$^2 \cdot$C^{-1} in the case of a conducting polymer-based EC device.[28,29] The best coloration efficiency value of any PV system reported to date is 170 cm$^2 \cdot$C^{-1}.[30]
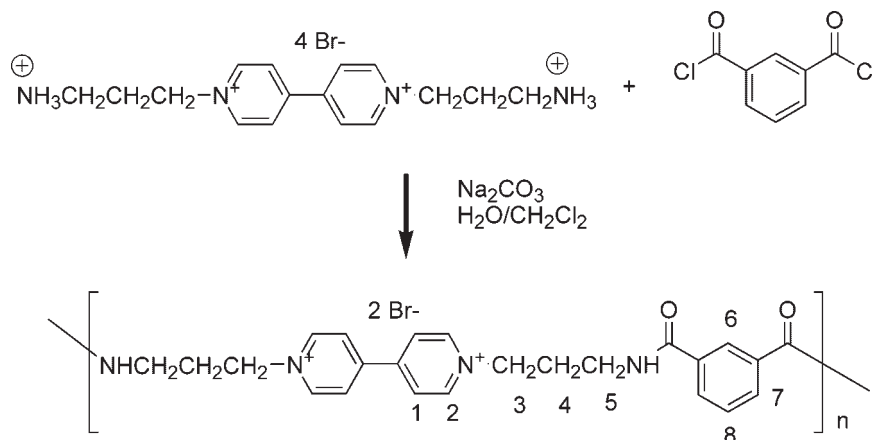
Change in the transmittance state from colorless to dark violet gives an optical density of

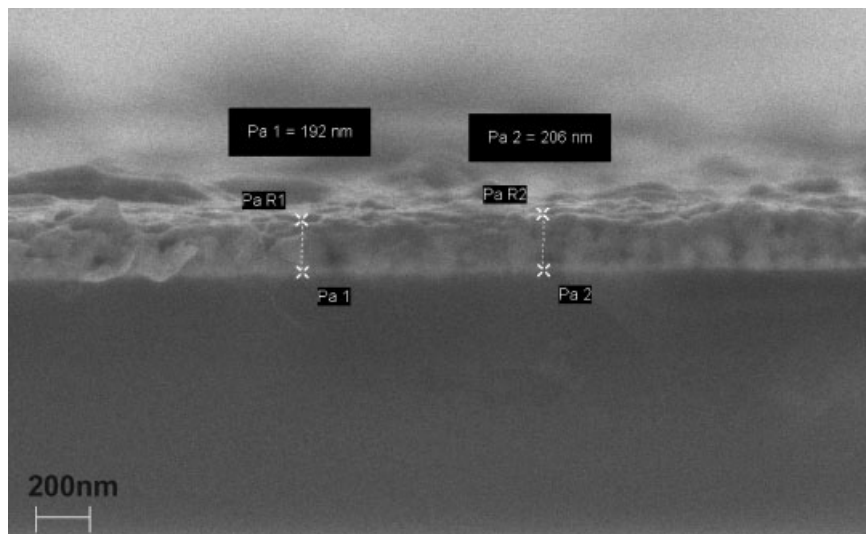$$\Delta OD(\lambda) = \log[T_b(\lambda)/T_c(\lambda)] \\ = 0.49 \tag{1}$$
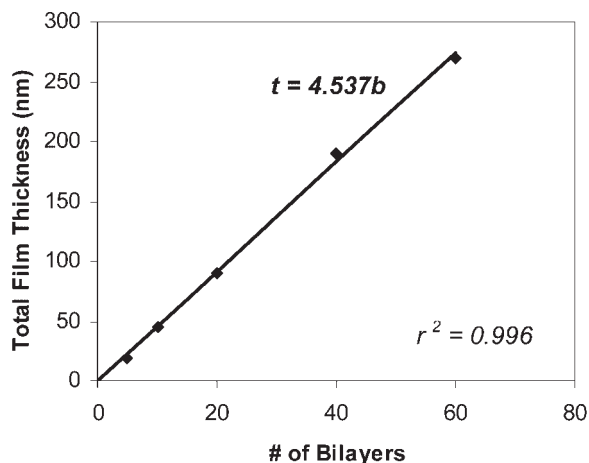
$$\eta(\lambda) = \Delta OD(\lambda)/Q_d \tag{2}$$
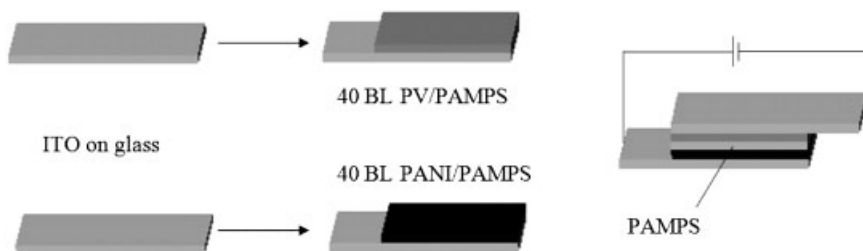
■ *Figure 1.* Solid-state dual ECD device from ISAM films of PV/PAMPs and PANI/PAMPs.

Scheme 2. Polymerization of N,N'-bis(δ-aminopropyl)-4,4'-bipyridinium bromide hydrobromide (APD) and isophthaloyl chloride (ISP).

Figure 2. An SEM image of the cross section of a 40 bilayer film of PV/PAMPs done at 5 kV shows the measurements of 192 and 206 nm.

Figure 3. Total thickness of PV/PAMPs films with increasing number of bilayers.

in which $Q_d = 8.6$ mC·cm^{-2} for the reduction step and is calculated as the area under the CV curve for the reduction peak for the scan rate of 100 mV·s^{-1}. The active working area of the film on the ITO electrode was 10 cm^2.

$$\eta(\lambda) = 57 \text{ cm}^2 \cdot \text{C}^{-1}$$

The absence of a second reduction peak in the CV curve, even at low scan rates, makes it difficult to calculate the charge required for the second reduction step from monocationic to the completely reduced state. As explained by Cinnsealach et al.,[16] the extinction coefficient (ε) of the reduced PV, assuming that every electron injected into the ITO electrode reduces a viologen moiety, can be expressed as:

$$\varepsilon(\lambda) = \eta(\lambda)F/1\,000$$
$$= 96.5\eta(\lambda) \quad (3)$$

in which F is the Faraday constant (96.5×10^3 C·mol^{-1}).

The value of ε for the reduced PV film at 515 nm was 5.5×10^3 M^{-1}cm^{-1}, which falls within the range of values reported by Monk et al.[1] for bipyridinium systems.

CV

A CV test was applied to a 40 bilayer film of PV/PAMPs (Figure 4). The results are similar to those of the PV-containing ISAM films studied by Delongchamp et al.[13] A sharp peak appears at −0.6 V, corresponding to fast first reduction, and the resulting monocationic radical shows dark violet color in the visible region. The redox activity and color changes reported here are representative of the wide class of viologens, so the color change that is observed is due to the change in the redox state of bipyridinium. The phthalic acid diamide unit in the PV could be electroactive, but does not undergo any redox process within the voltage range employed. The dark violet color remains during the reduction scan between −0.6 to −0.85 V, but changes to pale yellow due to the doubly reduced viologen at potentials higher than −0.9 V.
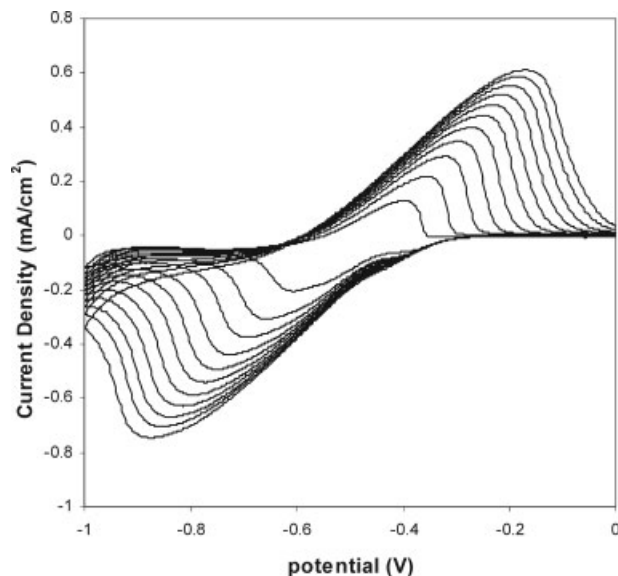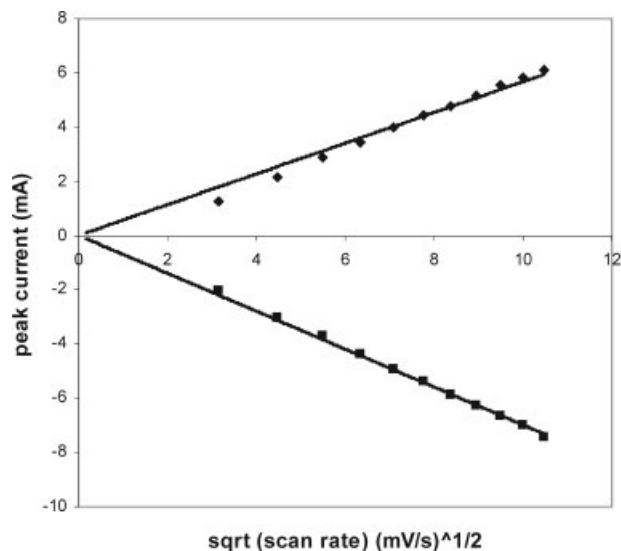
Figure 4. CV for the 40 bilayer film of PV/PAMPs in aqueous 0.1 M NaClO$_4$; reference was SCE. Active electrode of the film was 10 cm^2. Scan rate varies from 10 to 110 mV·s^{-1} and the arrow shows direction of increasing scan rate.

Figure 5. Peak current vs. square root of scan rate for oxidation and reduction peaks of the 40 bilayer film of PV/PAMPs in aqueous 0.1 M NaClO$_4$; reference was SCE. Active electrode of the film was 10 cm^2.

The second reduction peak, which corresponds to the yellow color, was not observed in the current CV scan of potential window from 0 to −1.0 V, but has been observed by several other groups at −1.0 V or higher for scan rates of 10 mV·s^{-1} or slower.[31] During the oxidation scan, the color changes from pale yellow to dark violet and finally back to original transparent state. Both reduction and oxidation peak current densities increase with the scan rate; this confirms that the reaction is diffusion controlled but slow (Figure 5). The PV/PAMPs films formed by ISAM fabrication technique are quite thin and display an increase in hysteresis for both peaks because of the internal resistance of the bulk film. As explained by Bird et al.,[32] the CV experiment of PVs in a wide potential window from 0 to −1.0 V or higher is chemically irreversible and the film degrades easily after a couple of scans with no peak, thus we limited the number of scans more negative than −1.0 V.

Peak current density varies linearly with the square root of scan rate for both oxidation and reduction, which confirms that the redox process is diffusion controlled and the whole film contributes to the change in color. Although the peaks skewed away from the potential, the peak current density linearly fits best with the square root of scan rate with an R^2 value of over 0.996 as compared to scan rate, which has a value of 0.72. This is one of the primary reasons that we observe such a high color contrast from the contribution of PV alone.

Diffusion controlled redox reaction is significant for the long-term stability of EC devices as it prevents charge trapping and film degradation with time, as observed with surface controlled redox processes. So, the whole thin ISAM film is accessible in this case and it also brings out the maximum contrast possible for PV. CV was done for films of different numbers of bilayers, and for all multilayer films the diffusion controlled rate of redox process remained constant.

Chrono-Amperometry

Chrono-amperometry was performed by stepping between −0.9 and 0.1 V (versus Hg/HgO) with 30 s per step and 60 s per cycle. 40 and 100 bilayer films (Figure 6) coated on ITO electrodes were used as working electrodes in a supporting electrolyte of aqueous 0.1 M KBr with a Pt wire as the counter electrode. For all the films, several cycles were performed sequentially before the data was measured. The current wave was invariant for at least 200 complete cycles. The maximum current density increased with increased bulk film thickness and shows a slower response time with increasing numbers of bilayers. The reduction step shown in Figure 6(a) has the final charge density (area under the current density trace) at 5 s of 70 and 22 mC·cm^{-2} for 100 and 40 bilayers, respectively. This ratio is not consistent with the increase in the number of bilayers and has also been observed by other groups studying the EC film properties of ISAM films of PV system.[13,33] Although the detailed explanation of this phenomenon is not completely clear yet, it is tentatively
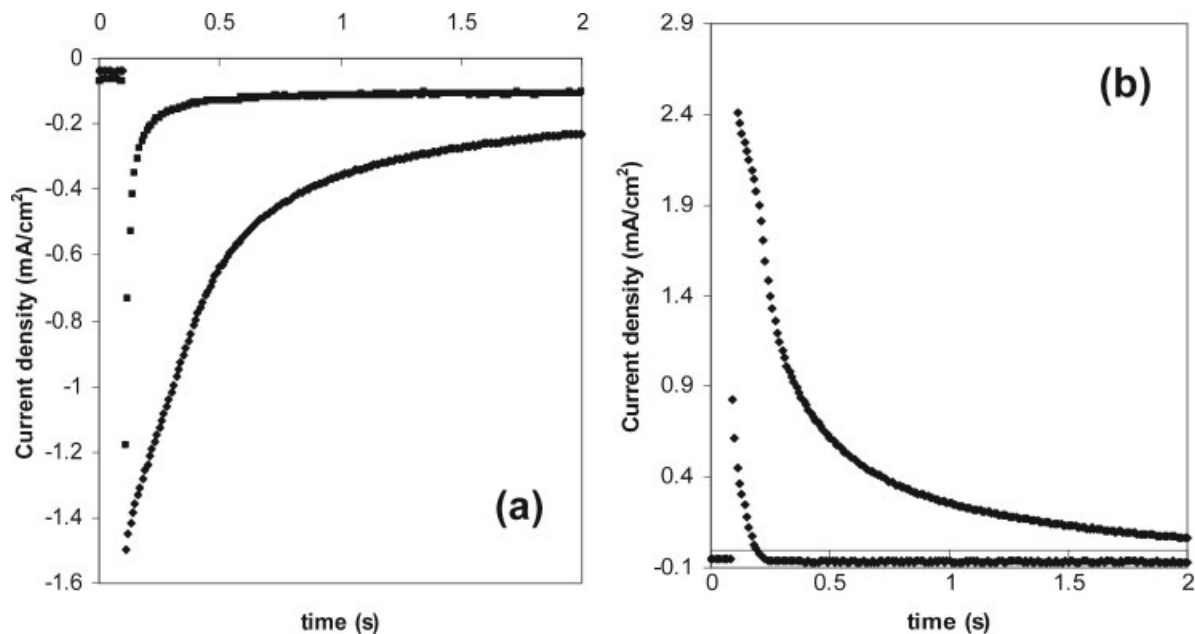
Figure 6. Reductive (a) and oxidative (b) current profile during switching from −0.9 to +0.1 V for PXV/PAMPS films of 40 and 100 bilayers. Active electrode surface area of the 100 and 40 bilayer ISAM film is 8.25 and 5.75 cm², respectively. Electrolyte was 0.1 M KBr and the reference was Hg/HgO.

attributed to the charge trapping in the case of thicker films.

Spectroelectrochemistry of EC Devices

Single-Type EC Devices

Spectroelectrochemical studies of the 40 bilayer PV/PAMPs film in 0.1 M NaClO$_4$ (aq.) were performed to study the transmission spectral changes with applied voltages at 0 V and from −0.6 to −1.0 V (Figure 7). The film changed from the colorless state of the PV with +2 oxidation state to the violet of the reduced +1 state to the transparent pale yellow of the completely reduced state. At λ_{max} 515 nm, a maximum transmission change of 61% was observed between the color states at 0 and −0.6 V of the mono-cationic state. On stepwise increase in the voltage from −0.6 to −1.0 V, the

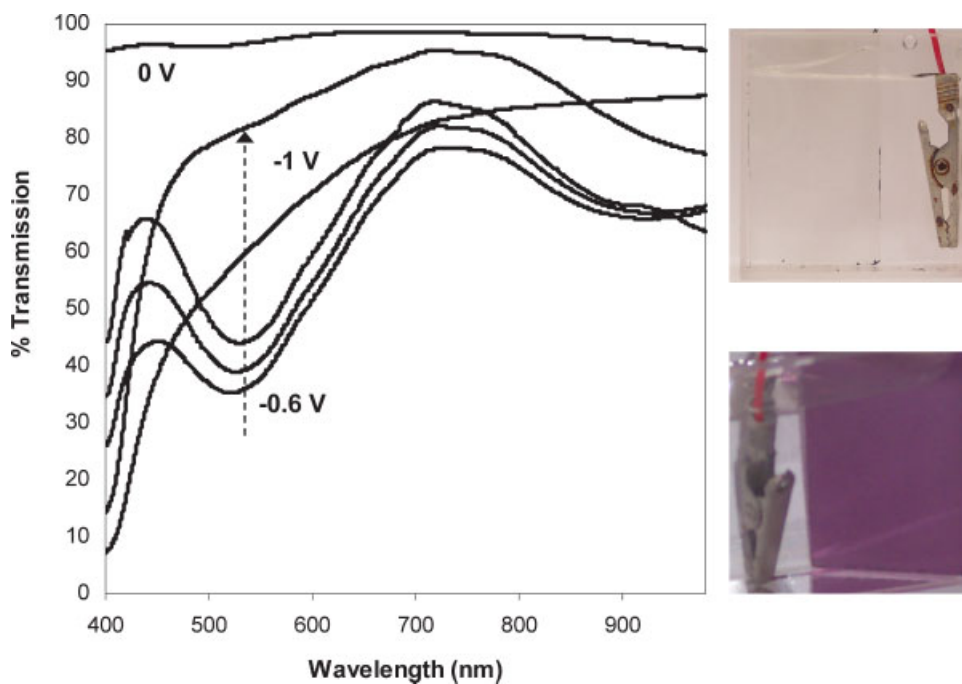observed change was 42% between dark violet and pale yellow color states. The second reduction peak was not observed in the CV experiment in the potential window from 0 to −1 V, but the yellow color attributed to this state

Figure 7. Transmission spectra of 40 bilayers of PV/PAMPs in 0.1 M NaClO$_4$ (aq.) solution with active electrode surface area of 10 cm². Applied voltage in direction of arrow is −0.6, −0.7, −0.8, −0.9, and −1.0 V. Digital photographs of bleached (colorless) and colored state (dark violet) of the 40 bilayer PV/PAMPs film.
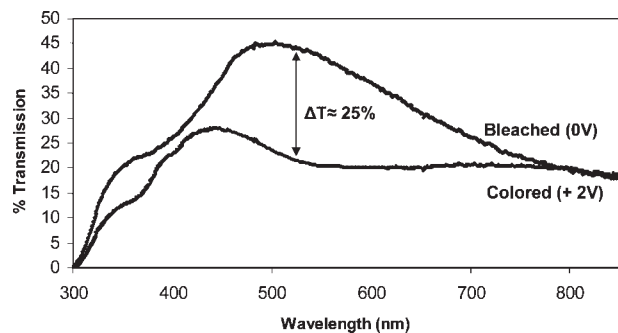
Figure 8. Transmittance change in the solid-state device of 40 bilayers PV/PAMPS and 40 bilayers of PANI/PAMPS on application of +2 V.
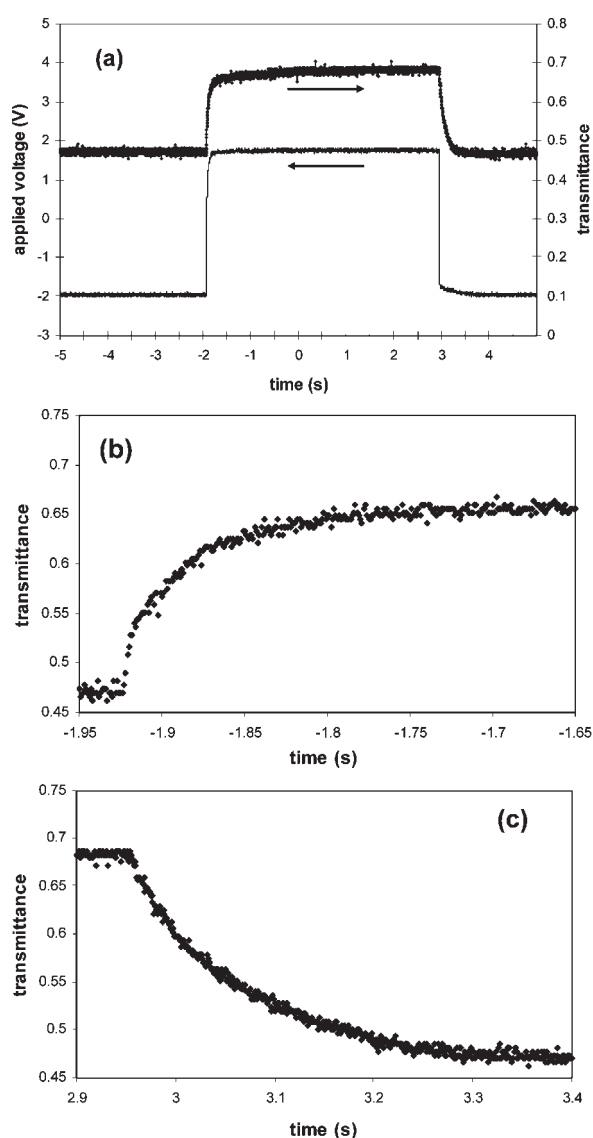

Figure 9. a) Switching speed curve for 40 bilayer solid-state device of PV/PAMPS and PANI/PAMS, transmittance as a function of time b) expansion of the coloration phase and c) expansion of the de-coloration phase.

was observed with spectroelectrochemistry during the voltage application of −0.9 V and higher. It is important to note that the film changes color to yellow, which is an unstable state for an extended period of time. For the long-term stability, the device should mainly work in the dicationic-monocationic transition. At −0.6 V, the transmission spectra remained unchanged, indicating that all the viologen moieties were reduced to the +1 oxidation state. Application of voltage higher than −1.5 V resulted in irreversible degradation to a permanently brown color. The contrast observed here for single electrochromic devices was on a par with results reported for PVs by other groups.[7,12]

Dual-Type EC Devices

A dual-type EC device (ECD) was fabricated with PANI as an anodically coloring material and PAMPs as the polyelectrolyte gel. PAMPs in diluted form (2×10^{-3} M) was used as the polyanion for ISAM film fabrication and in gel form (15 wt.-% in water) as the polyelectrolyte. The solid-state device was made up of 40 bilayers of cathodically coloring PV/PAMPs and 40 bilayers of anodically coloring PANI/PAMPs. The contrast of the 40 bilayer dual-type electrochromic device was 25% at 515 nm (Figure 8) on application of +2 V with respect to the PANI/PAMPs electrode. The maximum color change was observed at a wavelength similar to the one observed in salt solution (Figure 7). The contrast change for a 40 bilayer solid-state device is also on a par with the results shown by Lee et al.[34] for polythiophene-based devices.

Switching Speed in Solid-State

Switching of our devices was monitored over time with a He-Ne laser (632 nm) and photodiode as the square wave voltage (+2.0 to −2.0 V) was applied to the EC film. The solid-state device changed color from light green to dark violet and yellow at different voltages. As seen in Figure 9 the device had a switching time of 100 ms for coloration and a de-coloration time of 250 ms at 70% overall change in transmittance at switching voltages of 2.0 to −2.0 V; the optical switching reported is for the color change from light green to dark violet. As explained by Baioni et al., the difference in coloration and de-coloration time of the device is because of the different time constants for ejection/insertion of ions from/to the PV/PAMPs matrix.[35] The area of the color changing pixel in the solid-state device was 2 cm^2. To the best of our knowledge, this is the fastest PV switching ever reported. For better understanding of the coloration and decoloration times, an expanded view of the switching curve is also presented. For one of the best electrochromic displays of size 2.5 cm^2, Pettersson et al. reported coloration and de-coloration times of 300 and 400 ms, respectively.[36]

Conclusion

The use of the PV as an EC material provides a low reduction potential, good film forming ability and color tuning (colorless to dark violet to transparent yellow). Its solubility in water provides the advantage of easy processability using the ISAM film assembly method with PAMPs and the flexibility to incorporate other electrochromic materials that increase the overall contrast or develop multi-hue electrochromic devices. The high coloration efficiency (57 $cm^2 \cdot C^{-1}$) at low switching voltage (-0.2 V) and the ability to control the thickness of the bulk layer makes this approach unique. 40 Bilayers of PV/PAMPs on an ITO electrode show a contrast of 61% at 515 nm as the color changes from a highly transmissive colorless state to a dark violet to a transparent yellow.

Integrated PV-PANI dual EC devices produce more plentiful switching colors (blue, dark violet and yellow) than the simple PV device in electrolyte solution. The switching times for coloration and decoloration were 100 and 250 ms, respectively, at low switching voltages (-2.0 to $+2.0$ V) under ambient conditions.

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