

Diffuse color patterning using blended electrochromic polymers for proof-of-concept adaptive camouflage plaques

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ABSTRACT: A study using three different pairs of electrochromic polymers (ECPs) synthesized onto plaques by means of a modified vapor phase polymerization (VPP) technique is presented. Restriction of the respective polymerization times, allowed both faster and slower polymerizing monomers to be controlled, and produced blended plaques with visually diffuse interfaces. The ECPs within the blended plaques retain their individual electrochromic behavior and when encapsulated into an electrochromic device, show outstanding optical switching performance with little degradation evident over 10,000 cycles, coupled with a switching time of the order of 1 second. Blends also allow multiple diffuse color changes within an electrochromic device, due to the difference in oxidation potentials of the individual ECPs, making them candidates for adaptive camouflage use. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42158.

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INTRODUCTION

Spatial patterning of multi-deposited (conductive) ECPs is being investigated by many research groups^{1–7} in an effort to produce RGB (red-green-blue) color reproduction for display, lighting and light attenuation devices. In addition, the push for flexible/conformable devices has opened the door for organic based materials in lieu of the more traditional silicon/metallic based materials, which due to their inherent brittleness do not easily lend themselves to flexible applications. While many ECPs offer a level of mechanical elasticity, in general they are not soluble in aqueous based solvents without the addition of pendent side chains or additives such as polystyrene sulfonate (PSS).^{8,9} Traditionally ECPs have been prepared using two methods; “wet chemical” oxidative synthesis^{10,11} in which the monomer containing solvent is introduced and mixed with an oxidant containing solvent, or by electrochemical polymerization^{12–14} wherein the solvent borne monomer is electrically synthesized at the electrode face. Oxidative synthesis requires subsequent processing to then coat the polymer onto a substrate using a variety of methods such as; inkjet printing,^{15,16} screen printing,¹⁷ micro-contact printing,^{18,19} dip-pen lithography,^{20,21} or spray coating.²² For high resolution micro (or even nano) scale applications such as for photovoltaics^{17,23–26} and small-scale electronics,^{27,28} either direct printing of the polymer is required

or alternatively inkjet printing of the oxidant layer followed by vapor phase polymerization (VPP) may be utilized. Contrastingly, electrochemical polymerization results in the polymer being simultaneously synthesized and deposited *in-situ* onto conductive substrates.^{29,30}

When fine boundary resolution (sub-millimeter) is not of paramount importance, two relatively new techniques have been utilized to both simultaneously synthesize and coat substrates. The first is an adaptation of the electrochemical polymerization technique^{31,32} in which one (or more) monomer(s), electrolyte, and other additives are encapsulated into a sandwich structured cell with ITO electrodes.³³ Subsequent exposure to UV light creates a solid electrolyte gel and the monomer(s) is polymerized with the application of a voltage across the ITO electrodes. The technique³⁴ has been successfully used to create thin homopolymer electro-active layers, but more interestingly it has also been used to color-tune the layer by incorporating different ratios of the two monomers. Monomer diffusion through the electrolyte gel however takes several hours and the technique was only applied to relatively small substrates. The other technique is VPP^{27,35–37} which is an emerging technique that has the ability to overcome issues associated with polymer insolubility, as *in-situ* polymerization occurs on the substrate. Issues involving the simultaneous synthesis of more than one polymer have been

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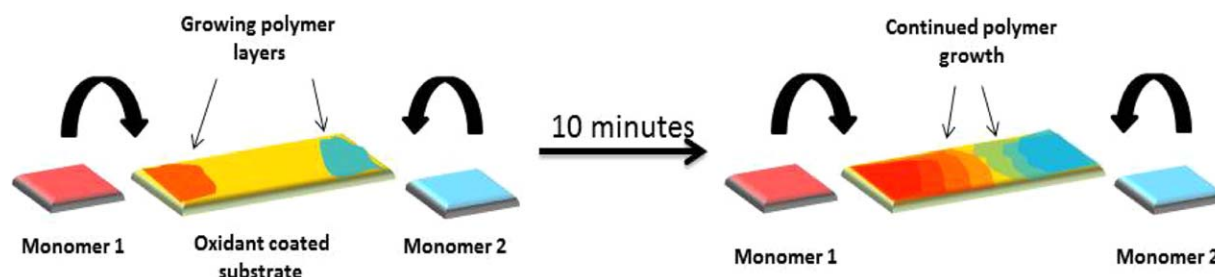


Figure 1. Schematic representation for the formation of polymer blends using the VPP technique. Monomer is transported in vapor form from wells and condensation occurs on the substrate. Differential monomer delivery can be achieved by means of controlling monomer: temperature, delivery time, or well aperture. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

addressed by modifying the VPP process.^{38–41} Recent work⁴² by our group has also demonstrated the successful deposition of multiple electro-active layers by sequentially introducing different monomer vapors into the polymerization process.

If the electro-active polymer patterning requirements need to be deposited onto large surfaces with the boundaries between the polymers needing to be visually diffuse, then the simultaneous or sequential introduction of two or more monomers using the VPP technique may provide for a facile solution. In this work, the creation of three different pairs of polymer blends with diffuse color boundaries were achieved using VPP in which two monomers were introduced into the chamber from opposing ends. This allowed a simple spatial pattern to form with a gradient overlap between the two polymers. The blending of two or more electro-active polymers without sharp edge separation has the potential to be used for adaptive camouflage electrochromic devices. Using this method diffuse multiple colored large area plaques were produced and then encapsulated to form proof-of-concept adaptive camouflage plaques. Such a process, although possible, would be difficult to achieve using conventional electrochemical techniques or oxidative polymerization followed by printing/spray/dip deposition methods. While there are a variety of methods available to control the polymerization of one monomer with respect to another, in this study the second monomer was simply introduced into the chamber after a predetermined time interval with respect to the first. The delay time was established based on the polymerization rates of each monomer.

EXPERIMENTAL

Materials

Iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), butanol, ethanol, poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (PEG-PPG-PEG, L-64, $M_w = 2900 \text{ g mol}^{-1}$), pyrrole and 2,2-bithiophene were obtained from Aldrich. 3,4-Ethylenedioxythiophene (EDOT) was obtained from Heraeus and the ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI) was obtained from Merck. All chemicals were used as received. Indium tin oxide (ITO) coated glass substrates were purchased from Zhuhai Kaivo Optoelectronic Technology Co.

VPP Blended Polymer Synthesis

The oxidant solution contained $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (13.8 wt %) and PEG-PPG-PEG (17.2 wt %) in BuOH. The solution was then spin coated (400B-6NPP, Laurell Technologies Inc.) at 1500 rpm

for 25 s onto ITO glass and then placed into the VPP chamber. Two monomers (either EDOT and pyrrole, or EDOT and bithiophene) were placed at opposing ends of the VPP chamber in 70°C crucibles without any vessel restriction, unless otherwise stated. The polymerization process was terminated when both ECPs overlapped in the middle and the characteristic yellow colored oxidant had disappeared. The ECP plaques were then washed with ethanol to rinse out the consumed oxidant.

Characterization

Elemental analysis was performed using X-ray Photoelectron Spectroscopy (XPS, SPECS, SAGE, Phoibos 150-HAS) fitted with a non-monochromatic Al anode of 200 W power, with a base pressure of 2×10^{-8} mbar. The electrochromic behavior of the individual ECPs within the polymer blends were observed by depositing the ECPs onto ITO coated glass substrates and incorporating them into an electrochromic test jig fitted with a Ag/AgCl reference electrode. The counter electrode was ITO glass. A VoltaLab PGZ100 All-In-One was used as an external voltage source for electrochromic switching analysis. The voltage applied to the ECP films was +1.5 V and -1.5 V unless otherwise stated. Final assembly (once the ECPs were deposited) was performed using a fully automated custom-built robotic jig (Janome JR 2400 N) which dispensed a UV-cure glue which was cured manually with a UV-wand (Dymax Bluewave 200, max. intensity 40 W/cm^2 , 280–450nm). Cell gap was pre-set to 100 μm . The electrochromic devices were back-filled under vacuum, by immersing them into a pyrrolidinium based ionic liquid electrolyte and venting the chamber to atmosphere. The optical switching performance of the encapsulated electrochromic devices were analyzed using a single-beam Hunterlab (Ultrascan UV-Vis-NIR) spectrophotometer or photodiode detector and LED emitter (both of which measured the photopic optical response centred at 550–560 nm) as described elsewhere,⁴³ and using cyclic voltammetry to cycle the devices. Both instruments measure the %T an observer would “see.” Switching time was defined as the time required to reach 90 % of the final overall optical transition.

RESULTS AND DISCUSSION

Background

Polymer blends were achieved using a modified VPP technique in which two different monomers were introduced into the VPP chamber from opposing ends. The oxidant coated substrate was centrally positioned within the chamber (see Figure 1). As each



Figure 2. Glass substrate highlighting a blend of PTh (far left) and PEDOT (far right) with a large diffuse central region composed of both polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

monomer was introduced the vapor slowly filled the chamber and polymerization was initiated at each of the opposing sides, and progressed inwards towards the centre. When the two propagating polymer fronts met (and overlapped) in the centre, the process was halted and the substrate removed from the chamber. The result was a diffuse interface at the centre and a gradient of the two polymers either side. The end result is a simple patterning of two polymers that retain their individual electrochromic behavior at the extremes with a blended response elsewhere. The inherent variability recorded for individual runs using such a simple system was viewed as a positive given the need for producing diffuse irregular boundaries for proof-of-concept adaptive camouflage plaques. By extension, this facile technique is open to the introduction of multiple monomers either simultaneously or sequentially to obtain a variety of different deposition mosaics.

Blended Polymer Synthesis

The VPP process is amenable to any monomer that is able to sublime or evaporate without suffering degradation of its monomeric unit. To validate the process two monomers, namely bithiophene and EDOT, were initially chosen as their ability to form individual stable thin films had already been verified in previous studies.^{44–46} Importantly, each resulting polymer possessed starkly different colors for easy visual confirmation. As such, it was anticipated that their ability to simultaneously form a horizontal polymer blend would be easily achieved. The oxidant employed was $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to ensure a fast polymerization pro-

cess, as this oxidant possesses high oxidation strength compared to other oxidants such as iron tosylate.⁴⁴ This was deemed necessary as a slow polymerization process would have allowed the two monomers to saturate the chamber resulting in poor spatial separation of the two forming polymers. The individual colors exhibited by the two ECPs in their neutral (as deposited) states made for simple identification as shown in Figure 2.

The polymer blend of PTh and PEDOT resulted in comparable polymerization areas being achieved, as the combination of each monomer's vapor pressure and polymerization rate were similar. However, when monomers have differing vapor pressures and/or polymerization rates the process becomes somewhat more complex, and measures need to be put in place to achieve suitable results. The more abundant and/or reactive monomer will dominate the polymerization process resulting in a "one-sided" blend or, in extreme cases, the polymerization of only one monomer. Differential restrictions can be applied to one or both of the monomers in order to slow the polymerization/deposition rate. Restrictions such as monomer volume, temperature and vessel aperture (*i.e.* vapor bottle-necking) are examples of the possible restriction techniques that can be applied.^{39,47} However, for this study a simpler restriction technique was utilized. A sequential time restriction process was implemented in which the slower polymerizing monomer was introduced into the chamber first for a predetermined time, followed by the addition of the second monomer. This technique was utilized to produce spatially separated polymer blends of PEDOT and PPy. Without this restriction initially produced films were completely dominated by the fast polymerizing pyrrole monomer. By polymerizing EDOT for 5 minutes before the introduction of pyrrole a blend of the two polymers was achieved and confirmed by simple visual observation. The distribution of the two resulting polymers was analyzed using XPS by comparing the sulfur to nitrogen ratio (*i.e.*, PPy contains nitrogen and PEDOT contains sulfur) across the sample.

XPS analysis was performed on the PEDOT/PPy blend at three different locations for sulfur and nitrogen in an effort to quantify the distribution of each polymer. The results shown in Figure 3 indicated that the formation was not as straight forward

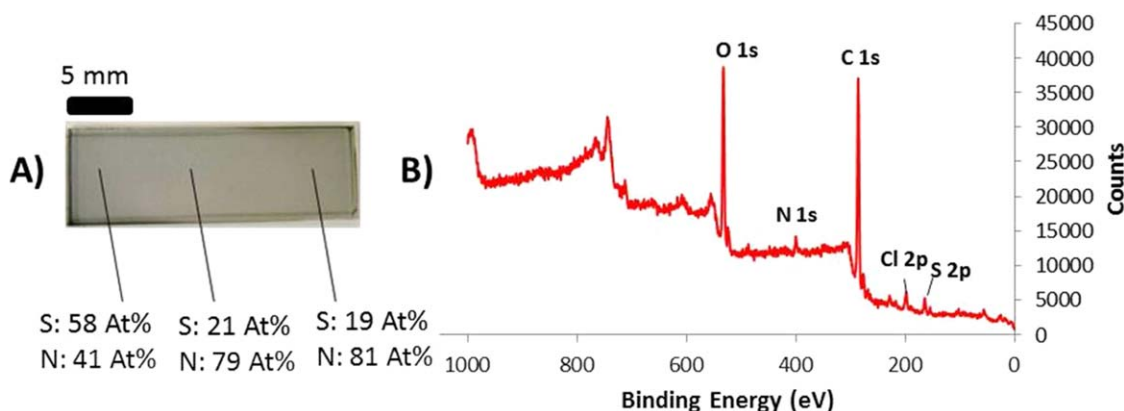


Figure 3. (A) Lateral S:N ratios for a PEDOT/PPy polymer blend made by polymerizing EDOT for 5 minutes before the introduction of pyrrole monomer and, (B) Example XPS spectra of a polymer blend of PEDOT/PPy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

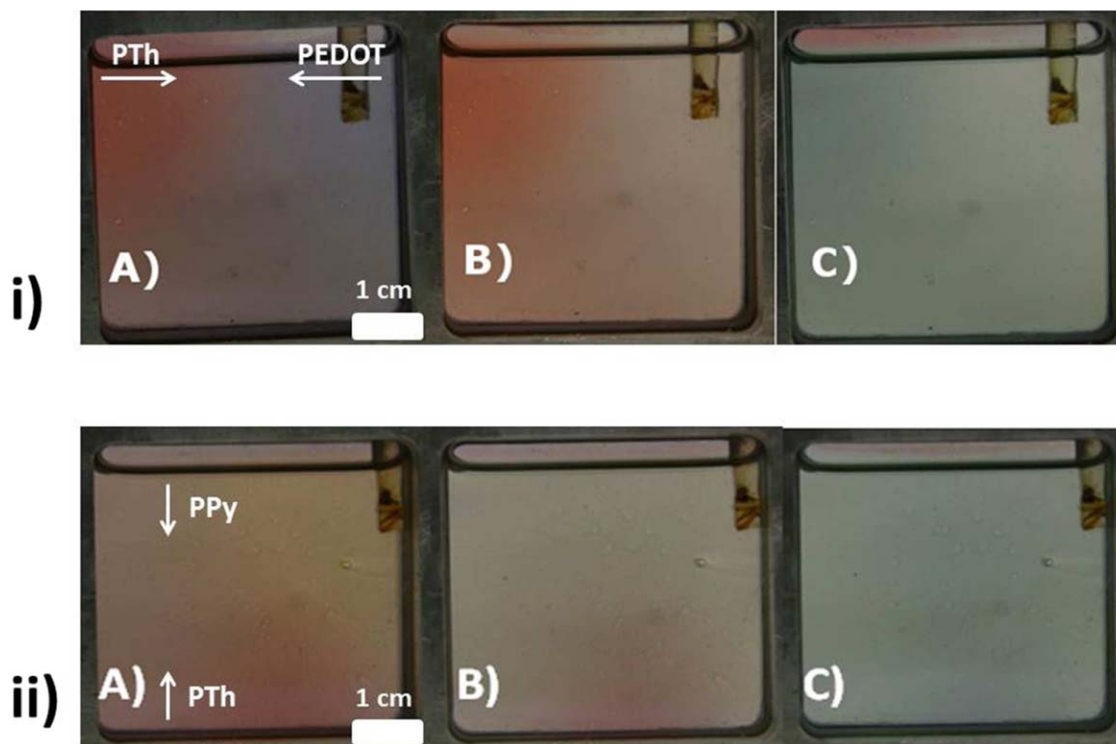


Figure 4. (i) Blend of PTh (left) and PEDOT (right) in A) reduced state, B) neutral state, and C) oxidized state; (ii) Blend of PTh (bottom) and PPy (top) in a) reduced state, B) neutral state, and C) oxidized state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as producing 100% of each polymer at the extreme ends with a gradient of each polymer elsewhere (i.e., central region). The XPS results show 19 At % sulfur at the pyrrole monomer side and 41 At % nitrogen at the EDOT monomer side. Rather than distinct homopolymer regions, a gradient of the two polymers was produced across the substrate. Interestingly however, rather than being a negative this diffuse blend process lent itself well to the fabrication of proof-of-concept adaptive camouflage plaques where hard color boundaries are seen as a distinct disadvantage.⁴⁸ Despite the observations shown by elemental analysis, the individual optical properties of PEDOT and PPy can be observed at the ends of the substrate in Figure 3, indicating that each polymer was able to actively switch in the presence of the other. What is unclear is whether the two monomers form a blend (i.e., two individual polymer chains residing next to each other) or a true co-polymer (i.e., each monomer unit residing on the one polymer chain [PEDOT]_m-[PPy]_n having an *m-n* ratio). The results shown in Figure 4 are inconclusive and the distinction between the formation of a blend of two homo-polymers, or indeed true co-polymerization is the subject of further study.

Electrochromic Behavior

The retention of the polymer's individual electrochromic behavior as well as an amalgamated response, regardless of whether the polymer is a blend or in fact a true co-polymer, opens up the possibility of multiple color changes within a single device. To investigate the electrochromic behavior of the polymer blends large (10 × 10 cm) plaques were fabricated. The initial small polymer blends fabricated using EDOT and bithiophene

did not require any form of monomer restriction, but an increase in polymerization time was noted for the larger plaques. As a consequence, it was necessary to time restrict the EDOT monomer delivery; EDOT was added to the chamber 5 minutes after the introduction of bithiophene. Polymerization was allowed to continue until the two ECPs (visually) met in the centre of the oxidant coated substrate (i.e., 20 minutes). The PEDOT-PTh blend was placed in the electrochromic test cell and voltages of −1.5 V and 1.5 V were applied. These voltages were sufficient to allow for the reduction of PEDOT and PTh (see Figure 4iA) through to the oxidation of both polymers (see Figure 4iC), with a “neutral” intermediate state (see Figure 4iB) in between. Figure 4ii) shows a blend of PPy and PTh which was created by initially polymerizing bithiophene and introducing pyrrole after 10 minutes. The same switching voltages, namely −1.5 V to 1.5 V were employed which allowed the polymers to be fully reduced (Figure 4 iiA), intermediate neutral (Figure 4 iiB) and fully oxidized (Figure 4 iiC). The various colored states in Figure 4 show the individual electrochromic behaviors of PTh, PEDOT and PPy as well as blended regions. This demonstrates the potential for *in-situ* spatial patterning of two (or more) ECPs without using complicated patterning techniques. In general, any combination of ECPs can be incorporated into the polymer blends as long as the monomer is able to form a vapor.

Electrochromic Device Performance

A potential problem with the concept of having two (or more) ECPs within the one electrochromic device is that different

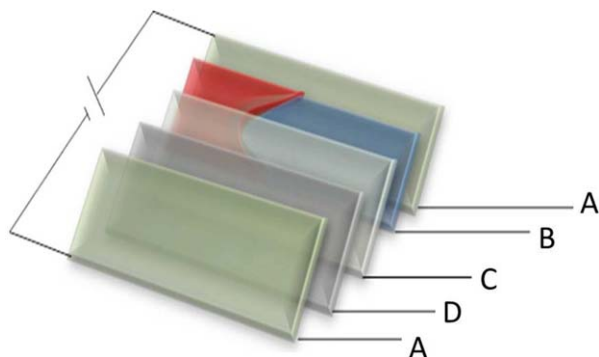


Figure 5. Schematic for proof-of-concept adaptive camouflage electrochromic device based on ECPs synthesised using the vapour phase polymerisation technique. (A) ITO glass, (B) Polymer blend of PEDOT and PTh, (C) Ionic liquid electrolyte, (D) PPy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymers require different oxidation and reduction potentials. A relatively high oxidation potential may be needed for one ECP, but this may degrade the second due to over-oxidation.⁴⁹ From a practical viewpoint, to see if such a situation would result in polymer degradation an electrochromic device was manufactured consisting of a polymer blend of PEDOT and PTh deposited on one electrode, with the counter electrode deposited with PPy. The device was encapsulated and the switching stability of the device investigated.

Figure 5 shows the schematic of the polymer blend electrochromic device with PEDOT and PTh on the working electrode and PPy deposited on the counter electrode. Before testing this device the stability of a PEDOT (working electrode) and PPy (counter electrode) device was benchmark tested. Based on the cyclic voltametric analysis (refer Supporting Information Fig S2) a voltage range between -1.5 V and 1.5 V was deemed appropriate to affect a full optical switch, while also probing the electrochromic cycling stability of the device (the % Transmittance change over the voltage range is given in Supporting Information Fig S3). Cyclic voltammetry indicated no discernible over-oxidation of either polymer and no optical transmission or switch time degradation was evident after 10,000 switches (refer Supporting Information Fig S1: Dark-Bleach 1.3 s and Bleach-Dark 1.1 s). Therefore, based on this result any degradation observed in the PEDOT + PTh/PPy device could be assigned to the polymer blend (i.e., PEDOT + PTh), and in particular the PTh.

The photically weighted (centered at 550–560 nm) optical switching (i.e., time taken to reach 90% of the full optical transition) for the PEDOT+PTh/PPy shown in Figure 6A was approximately 1 second for each transition and is similar to other EC devices.^{14,30} This is a relatively quick switching time when taking into account that the optical switch recorded herein was $T_{90\%}$ (rather than $T_{50\%}$) and the large size of the EC device itself (10×10 cm), as large devices are known to suffer an “optical halo effect”⁵⁰ when switching due to charge ingress/egress originating from the perimeter of the device. However, over the relatively short switch time of *ca.* 1 second this perceived optical effect was minimal. An optical shift was observed

after 10,000 switches, with a small downward shift for both the bleached and darkened states noted. The small downward (or upward) shift is colloquially known as device “warm up” and is due to a new doping equilibrium that differs from the “as synthesized” condition. This is as a result of the diffusion of electrolyte into the polymer interacting with the doping anions. A small degradation in the optical switch (*ca.* 2.5% overall change) was noted after 10,000 cycles and based on the benchmark result this was attributed to the degradation of PTh. To further elucidate the mechanism behind the optical change, the current ingress/egress versus time was investigated for the 1st and 10,000th cycle. The total current flow resulting from an optical switch is the result of; capacitive, Faradaic and (small) parasitic components.⁵¹ Given that the capacitive and parasitic components are unlikely to change unless the geometry of the device changes, any change in the overall current is thus the result of a change in the Faradaic current. Changes in Faradaic are an indirect measure of polymer degradation. A small decrease in both the oxidation and reduction currents were noted (see Figure 6B), and this is consistent with conjugation (scission) degradation of the PTh polymer which has been

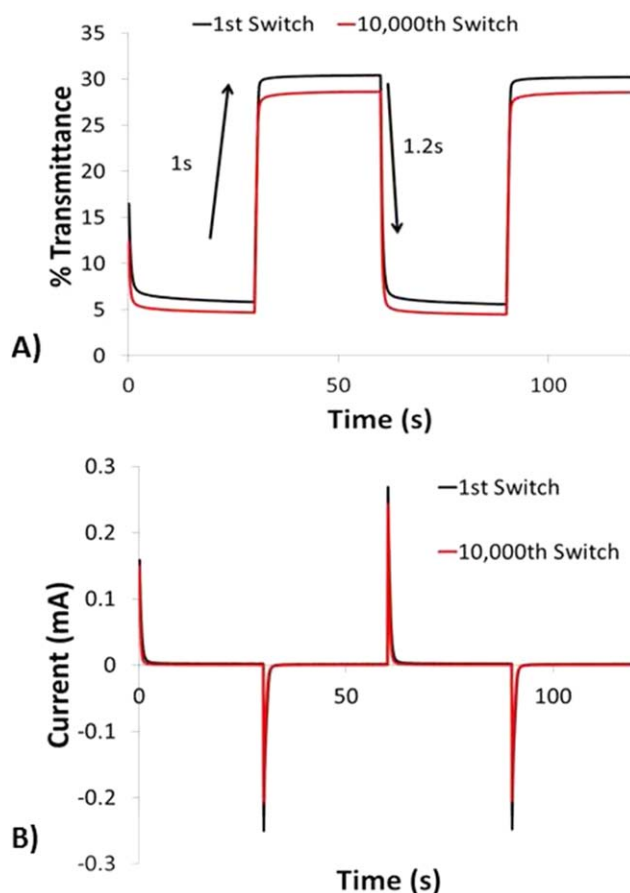


Figure 6. (A) Change in photopic transmittance for the blend PEDOT + PTh/PPy device versus time with an applied voltage (square wave from 1.5 to -1.5 V). (B) Current versus time chromatograph with a square waveform (1.5 to -1.5 V) applied to the polymer blend device. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

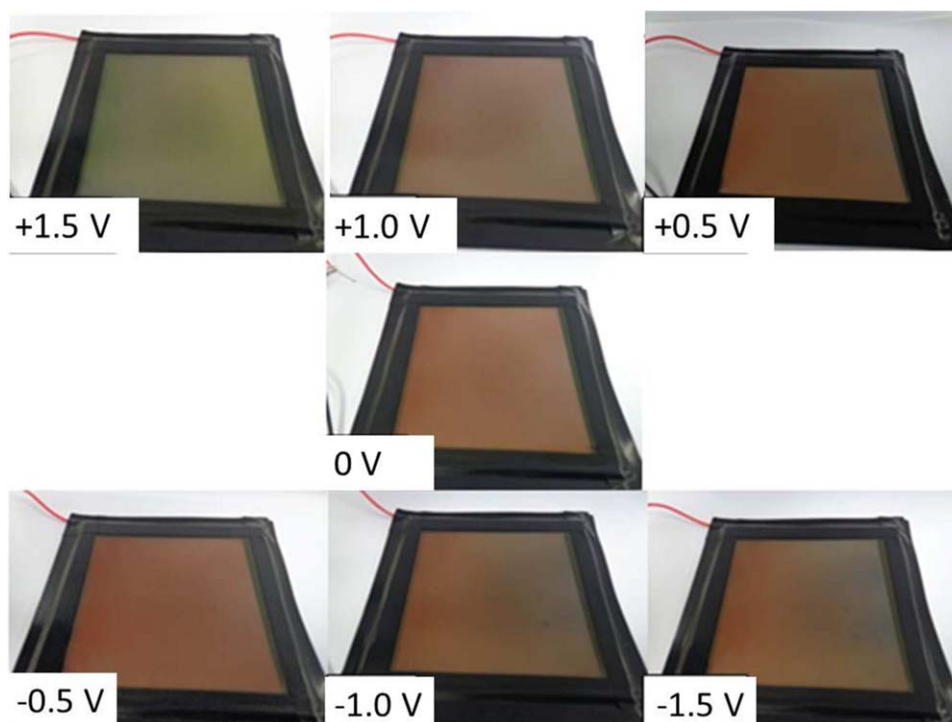


Figure 7. PEDOT+PTh/PPy device (10×10 cm active area) at different voltages, highlighting the different color changes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reported by others.⁵² Given that the polymer blend was synthesized under ambient conditions with no humidity control, rather than under vacuum conditions, a small 2.5% reduction in optical performance after 10,000 switches was deemed acceptable.

A voltage from -1.5 to $+1.5$ V was applied to the PEDOT + PTh/PPy electrochromic device and the color changes are given in Figure 7. The sandwich structured device highlights the different color patterns possible due to the variation in oxidation/reduction potentials for each homopolymer (and blend) region. The oxidation potential of PTh is higher than both PEDOT and PPy as its oxidized state was only observed at the highest voltage (i.e., blue/green at 1.5V), whereas the transparent sky blue state (i.e., oxidized) of PEDOT was apparent at voltages greater than -0.5 V. Therefore the polymer blend, coupled with changes in applied voltage, has been able to produce a device that has multiple blended colored states.

CONCLUSION

The facile polymer blend technique using a modified VPP procedure provided a simple method for introducing additional polymers onto the same plaque. This negates the need for patterning and masking techniques to create patterned multi-colored electrochromic devices. Polymer blends synthesized using monomers with comparable polymerization rates were easily achieved and a (simple) time restriction technique was applied when this was not the case. Small-scale polymer blends of PEDOT and PTh were created without any restrictions being applied to the monomers, whereas blends of PEDOT and PPy were synthesized by restricting the polymerization time for the

pyrrole monomer. Elemental analysis of PEDOT/PPy blends showed that a gradient existed across the film which was dominated by PPy. There were regions in which the individual polymers retained their electrochromic properties as well as evidence for blended regions. This allowed for the production of multiple optical colors within the devices. The PEDOT + PTh/PPy device showed minimal degradation over 10,000 cycles, recording a loss of only *ca.* 2.5% in optical switch range and no change in the optical switch time.

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