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Acrylated Poly(3,4-propylenedioxythiophene) for Enhancement of Lifetime and Optical Properties for Single-Layer Electrochromic Devices

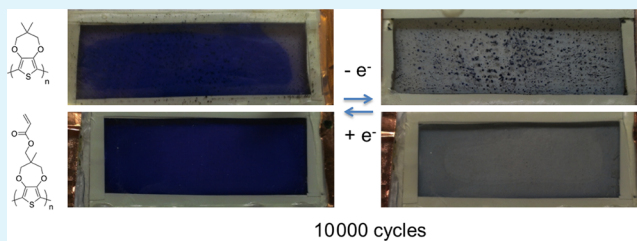
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S Supporting Information

ABSTRACT: We utilized our in situ method for the one-step assembly of single-layer electrochromic devices (ECDs) with a 3,4-propylenedioxythiophene (ProDOT) acrylate derivative, and long-term stability was achieved. By coupling the electroactive monomer to the cross-linkable polymer matrix, preparation of the electrochromic ProDOT polymer can occur followed by UV cross-linking. Thus, we achieve immobilization of the unreacted monomer, which prevents any degradative processes from occurring at the counter electrode. This approach eliminated spot formation in the device and increased stability to over 10 000 cycles when compared to 500 cycles with conventional ProDOT devices wherein the monomer is not immobilized. The acrylated electrochromic polymer exhibits similar electrochromic properties as conventional ProDOT devices, such as photopic contrast (48% compared to 46%) and switch speed (both 2 s). This method can be applied to any one-layer electrochromic system where improved stability is desired.

KEYWORDS: electropolymerization, electrochromic, conjugated polymer, electrochromic devices, displays, windows



INTRODUCTION

Electrochromics alter light transmission through charge injection and removal.¹ Electrochromic materials are gaining popularity because of their rapid response speed and high contrast.^{2,3} Current commercial applications, such as electrochromic mirrors and smart windows, are primarily small-molecule organic or inorganic in composition.⁴ Recent high-profile commercial applications include Boeing's use of electrochromic windows in their 787 Dreamliner to eliminate window shades and Mercedes Benz's use of an electrochromic roof panel in the SLK.⁵ Organic ECDs are regarded as the next generation of eyewear, windows, displays, and even fabric.^{6–15} These devices are possible because of the use of conjugated polymers (CPs), which were originally discovered in the 1970s. CPs rely on the extended π conjugation along the polymer backbone for their spectral absorption. The energy gap between the HOMO and LUMO for CPs changes with an applied voltage because the material changes from an insulator to a semiconductor. This results in absorption shifts and visible color changes, thereby offering a full visible spectral range of colors for these polymers. These properties make CPs of considerable interest for devices where the optical modulation of transmittance and/or reflectance is desired.

Poly(3,4-ethylenedioxythiophene) (PEDOT) was first reported as an electrochromic material in 1994. When prepared, it yielded an electrochromic polymer that gave a transition from dark blue in its neutral state to a light sky blue in its oxidized

state.¹⁶ Poly(3,4-propylenedioxythiophene) (PProDOT) and its derivatives have shown the ability to yield higher contrasts than PEDOT.¹⁷ PEDOT has a six-membered planar ring, but ProDOT's seven-membered ring is non planar. This results in increased spacing along the polymer backbone, reducing the stacking of the polymers and thus reducing electron chain hopping. In doing so, the absorption in the near-infrared (NIR) is reduced along with the tail into the visible region, making them more transmissive in their oxidized state. By modifying the R groups on P(ProDOT), the color transitions can be tuned across the visible spectrum. For example, 2,2-PProDOT-Me₂ transitions between purple and sky blue, whereas 1,3-PProDOT-tBu₂ transitions between yellow and sky blue.¹⁸ Furthermore, Reynolds et al. reported black using EDOT in a donor–acceptor polymeric system.¹⁹ Previously reported acrylated ProDOTs and PEDOTs include, for example, 3,4-propylenedioxythiophene-methacrylate (ProDOT-MA), which was used as a means for photopatterning electrochromic devices.^{20–22} The patterning was accomplished by polymerizing the conjugated polymer by heat, and then the device was photopatterned by UV irradiation. Also, Reynolds et al. recently reported a methacrylate-substituted ProDOT copolymer for photopatterning applications.²³

Received: October 22, 2013

Accepted: January 17, 2014

Published: January 17, 2014



Our group previously reported the in situ method for the fabrication of electrochromic devices (ECDs) that simplified the assembly of ECDs by allowing open-air fabrication, low waste, and shorter assembly steps and times.^{24,25} With this in situ method, a single layer is prepared between two optically transparent electrode (OTE) substrates, which reduces the practice of processing electrochromic devices to a simple lamination procedure. This new procedure can replace the need for the previously reported procedure of a dual-layer ECD approach.^{26,27} Recently reported in the literature was the demonstration of high-throughput screening of ProDOT monomers (using the in situ method) whose polymers are of a single absorption within a single ECD, which resulted in copolymers of different feed ratios exhibiting the full spectral range of the subtractive colors from yellow to blue.²⁸

Long-term stability of in situ ECDs is imperative to the commercialization of its many promising applications. Previously, the stability of the in situ ECDs heavily relied on the unpolymerized monomers not aggregating on the electrode. When a defect is present in the device, spotting issues were occasionally seen within the ECDs after several hundred switching cycles that exacerbated over time on some of the devices. The hypothesis was that these spots were caused by unreacted monomers because, with the in situ method, polymerization occurs after device assembly by electrochemically polymerizing the monomer in the gel electrolyte. The leftover monomers (ca. 95.5%)²⁴ diffuse²⁸ toward these nucleation spots on the counter electrode, causing the spots to increase in size over time. The sites where these spots occur are a matter of debate, but they are most likely occurring at a defect site on the indium tin oxide (ITO) coating, as it is only occasionally seen considering the area of the substrate. However, by using a poly(3,4-propylenedioxythiophene) P-(ProDOT) modified with an acrylate group (ProDOT-Ac), the conjugated polymer and unreacted monomers can be UV cross-linked at the same time as the gel matrix, integrating them into a tightly cross-linked network that prevents any migration of unreacted materials, thus increasing stability and overall optical quality.

■ EXPERIMENTAL METHODS

Materials and Methods. Lithium trifluoromethanesulfonate (LITRIF), dimethoxyphenylacetophenone (DMPAP), propylene carbonate, poly(ethylene glycol) diacrylate ($M_n = 700$), and acetonitrile were purchased from Sigma-Aldrich and were used as received. Indium-doped tin oxide (ITO) glass was purchased from Delta Technologies and cleaned by sonication in acetone prior to use. The electroactive monomer, 2,2-dimethyl-3,4-propylenedioxythiophene (ProDOT-Me₂), was synthesized using a transesterification ring closure starting with commercially available 3,4-dimethoxythiophene and 2,2-dimethylpropane-1,3-diol (Sigma-Aldrich) according to a literature procedure.¹⁷ Acryloyl chloride, 1,1,1-tri(hydroxy-methyl)ethane, and *p*-toulenesulfonic acid (pTSA) for preparation of ProDOT-Ac were used as purchased from Sigma-Aldrich. Toluene (Sigma-Aldrich) was cannulated from our dry solvent/degassing system (S. G. Waters). Dichloromethane and triethylamine were distilled before use and were purchased from Sigma-Aldrich. Sealant (UVS 91) was purchased from Norland Optics and used as received. Conductive copper adhesive tape was purchased from Newark Electronics and used as received.

Gel Polymer Electrolyte. Traditional devices were prepared using 5 g of propylene carbonate, 5 g of poly(ethylene glycol) diacrylate ($M_n = 700$), 1 g of lithium trifluoromethanesulfonate (LITRIF), and 17.5 mg of 2,2-dimethoxy-2-phenyl-acetophenone (DMPAP), which were added together and sonicated for 15 min until dissolved.

Electrochromic Device Assembly. Two electrochromic devices were fabricated using the in situ assembly approach. First, ProDOT-Ac monomer was added to the gel electrolyte in a 7.5 wt % ratio and drop-cast onto the ITO-coated glass substrate, and another piece of ITO-coated glass substrate was put on top. A potential of +3 V was applied to the device for 30 s, polymerizing the monomer in the liquid state. The device was then cured using UV light at 320 $\mu\text{W}/\text{cm}^2$ intensity for 5 min. The device was cycled between ± 2 V for switching the electrochromic device between the oxidized and neutral states for stability testing. Second, the control device consisted of 2.5 wt % ProDOT-Me₂ added to the gel electrolyte and was then sandwiched between two ITO substrates using UV-curable glue as an edge sealant and copper tape leads. Then, the device was cured for 5 min using UV light at 320 $\mu\text{W}/\text{cm}^2$, and a potential of +3 V was applied to the device for 30 s to polymerize the monomer in the solid state. The device was then cycled between ± 2 V for switching the electrochromic device between the oxidized and neutral states for stability testing.

Equipment. All electrochemistry was performed using CHI 400 or CHI 660A potentiostats. Spectroelectrochemical studies were carried out using a CARY 5000 UV-vis-NIR spectrophotometer. Colorimetric measurements were obtained by a PR-670 SpectroScan spectroradiometer (Photo Research, Inc.). Cyclic voltammetry for ProDOT-Me₂ and ProDOT-Ac was performed using 0.1 M LITRIF/ACN electrolyte solutions containing 10 mM monomers. A platinum button electrode (2 mm diameter) was chosen as the working electrode. A platinum flag (0.5 cm^2) was used as the counter electrode, and a silver wire was used as the pseudoreference electrode. Potential was scanned between -0.6 and $+1.6$ V for four cycles at a scan rate of 100 mV/s. Both ^1H and ^{13}C NMR were performed on a Bruker DMX500 high-resolution digital NMR spectrometer. Gas chromatography and mass spectrometry was carried out on a Hewlett-Packard 6890 series gas chromatography mass spectrometer. Infrared spectroscopy was performed on a Nicolet Magna 560 FTIR spectrometer.

Synthesis. (3-Methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methanol (ProDOT-OH) (5). 3,4-Dimethoxythiophene (4 g, 27.8 mmol) was taken with 500 mL of toluene, and to this was added 1,1,1-tri(hydroxy-methyl)ethane (4.32 g, 36.10 mmol) followed by *p*-TSA (0.52 g, 2.78 mmol). The reaction mixture was refluxed with a Soxhlet over 4 Å molecular sieves under a continuous flow of argon for 12 h. Excess toluene was evaporated, and the greenish black residue was extracted with ethyl acetate, washed repeatedly with water, and dried over magnesium sulfate. The ethyl acetate was then removed under vacuum. The crude product was purified by silica gel column chromatography eluting with hexanes/ethyl acetate mixture (80:20) to give a colorless viscous oil that solidified to a white solid. Yield: 4.6 g (86%). ^1H NMR (500 MHz, CDCl_3) δ 0.95 (s, 3H), 1.70 (s, 1H), 3.73 (d, $J = 12$ Hz, 2H), 3.74 (s, 2H), 4.08 (d, $J = 12$ Hz, 2H), 6.48 (s, 2H). ^{13}C NMR (CDCl_3) δ 17.18, 43.93, 65.62, 76.60, 105.77, 149.56. GC/MS (m/z): 200.

(3-Methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methyl Acrylate (ProDOT-Ac) (7). Under argon in a three-necked flask, ProDOT-OH (0.26 g, 1.3 mmol) was added to 30 mL of freshly distilled dichloromethane (DCM), and 0.36 mL of freshly distilled triethylamine (TEA) (0.26 g, 2.6 mmol) was then added to the solution. The solution was then cooled to 0 °C, and 0.16 mL of acryloyl chloride (0.18 g, 2 mmol) was added dropwise. After 2 h, the reaction was extracted with 30 mL of water and 3×30 mL of DCM. The organic layer was dried over MgSO_4 , filtered, and concentrated under vacuum. The crude product was purified using column chromatography with a 1:1 DET/hexanes solvent system. Then, the pure fractions from the column were further purified by recrystallization using ethanol as the solvent, yielding dense white crystals. (0.24 g, 75%). mp 59.5–60 °C. ^1H NMR (500 MHz, CDCl_3) δ 6.52 (s, 2H), 6.45 (dd, $J = 17.3, 1.3$ Hz, 1H), 6.18 (dd, $J = 17.3, 10.5$ Hz, 1H), 5.89 (dd, $J = 10.4, 1.3$ Hz, 1H), 4.31 (s, 1H), 4.08 (d, $J = 12.0$ Hz, 1H), 3.79 (d, $J = 12.0$ Hz, 1H), 1.03–1.00 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.9, 149.6, 131.1, 128.1, 105.8, 76.3, 66.4, 42.7, 17.2. GC/MS (m/z): 254. FT-IR (KBr, cm^{-1}): 3113, 2962, 2890, 1720, 1637, 1481, 1459, 1408, 1389, 1375, 1299, 1213, 1192, 1170, 1028, 1000, 981, 971, 873, 808, 782, 771, 667.

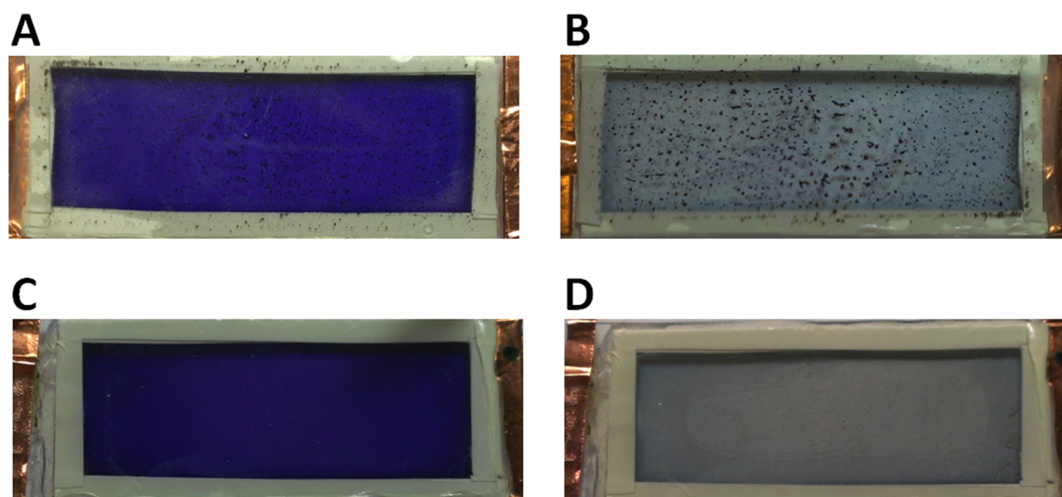


Figure 1. (A, B) Control device ($1.9 \times 5.1 \text{ cm}^2$ with an active area (polymer area) of $1.4 \times 4.2 \text{ cm}^2$), PProDOT-Me₂, in the neutral and oxidized states, respectively, showing spotting after 4000 cycles. (C, D) Neutral and oxidized states of PProDOT-Ac, respectively, after 10 000 cycles.

RESULTS AND DISCUSSION

The in situ procedure used in our lab has simplified the assembly of ECDs because of its open-air fabrication, reduced

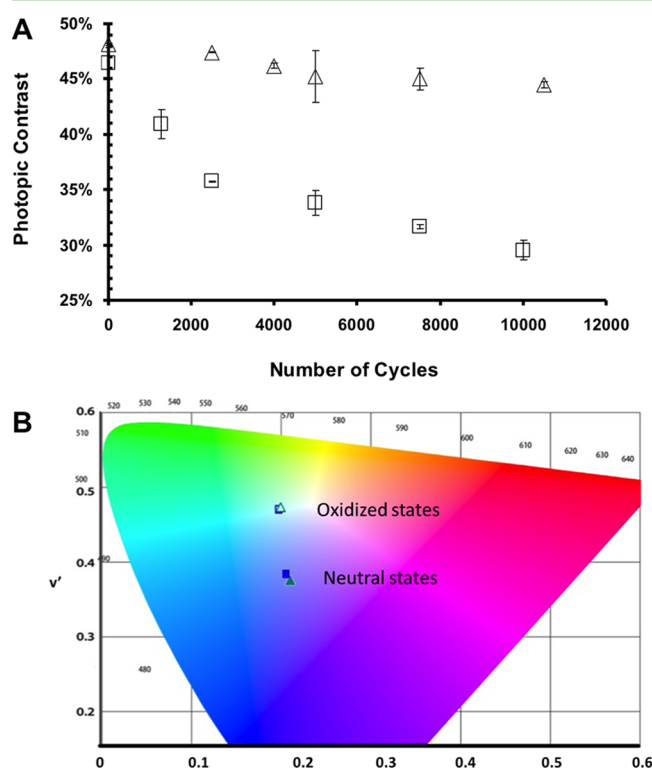


Figure 2. (A) Photopic contrast for PProDOT-Ac (shown in triangles) with an initial photopic contrast (48%) higher than PProDOT-Me₂ (46% shown in squares) and a drop of only 3% in the contrast over 10 000 cycles. (B) Color coordinates of PProDOT-Ac and PProDOT-Me₂ in the neutral and oxidized states.

waste, and application of a single layer between OTEs in what could be envisioned as a standard lamination procedure. Most PProDOT-Me₂ devices perform flawlessly without spotting, but, as seen in Figure 1A,B, spotting does occur in some devices after cycling for a period of time. For optical consistency and long-term stability of ECDs, an alternative method was studied.

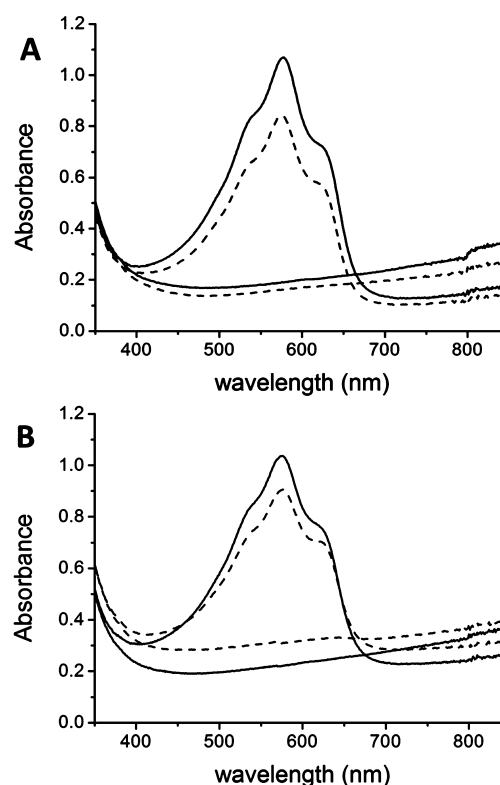
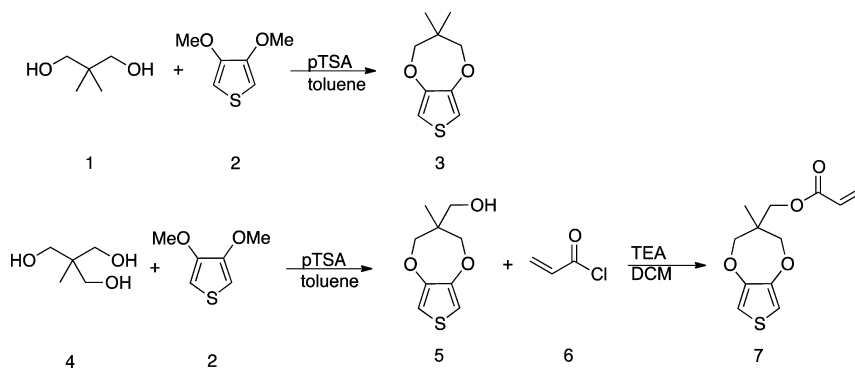


Figure 3. UV-vis spectra of PProDOT-Ac (solid) and PProDOT-Me₂ (dashed) initially (A) and after 10 000 cycles (B).

The hypothesis was that if an acrylate group was added to the monomer then the unreacted monomers could be locked into the gel matrix upon UV curing. This would, in turn, prevent migration of the monomers to the counter electrode, thereby preventing nucleation and growth, provided the spots are due to unreacted monomer. The comparison between the devices prepared from the control, PProDOT-Me₂, and an acrylated PProDOT (PProDOT-Ac) can be seen in Figure 1. The PProDOT-Ac device in Figure 1C,D shows no evidence of spotting after 10 000 cycles. After 10 000 cycles, the PProDOT-Ac devices were still operating exceptionally; 10 000 cycles was chosen as our upper bound because it is a sufficient lifetime for

Scheme 1. Synthesis of Control Compound 3 and Acrylated ProDOT Compound 7



Scheme 2. Reactions Occurring within the Single Layer of a Device during in Situ Electrochemical Polymerization and Subsequent Photochemical Cross-Linking

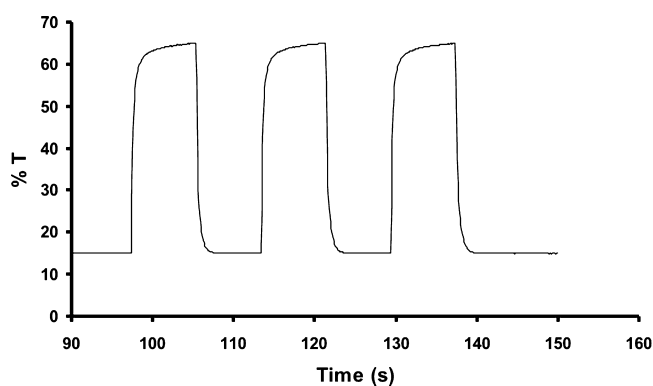
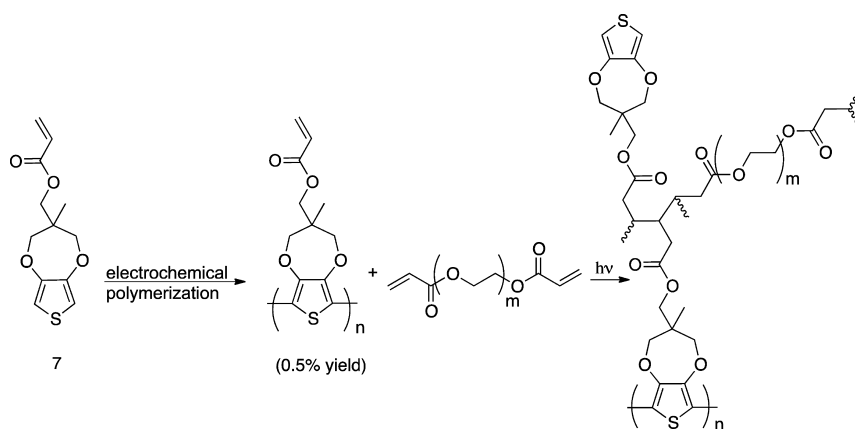


Figure 4. Switching speed for PProDOT-Ac.

smart glass and eyewear applications. For example, if a window application was cycled once a day, then it would last 27 years, and for sunglass applications that were cycled 10 times per day, it would last close to 3 years.²⁹ The PProDOT-Ac devices were optimized for film quality and contrast at 7.5% w/w compared to the control, PProDOT-Me₂, at 2.5% w/w. This highlights the low waste and low cost of the in situ procedure resulting from the small concentration of monomer needed for assembling devices.

The photopic contrast is improved initially in the PProDOT-Ac devices, as seen in Figure 2A, with an initial photopic contrast of 48% as compared to the control's initial contrast of 46%. However, the benefit of using the acrylated ProDOT is seen over the course of 10 000 cycles, where only a 3% drop in

photopic contrast is observed. The PProDOT-Me₂ devices averaged a 14% drop in contrast over 10 000 cycles, where contrast is affected because of deleterious side reactions on the counter electrode. Figure 3A,B shows the loss in initial contrast after 10 000 cycles. The cycling experiments were performed under the most extreme conditions with constant switching over a continuous period of 24 h that was only stopped to take contrast measurements. The color of the PProDOT-Me₂ and PProDOT-Ac devices are almost identical, as seen in Figure 2B. The color coordinates were determined using the CIE Lu'v' color coordinates (u', v') for each device. The color of the PProDOT-Ac devices were purple with u', v' color coordinates of 0.2118 and 0.3737, respectively, in the neutral state. The oxidized state was clear, as seen with other PProDOTs and similar to the PProDOT-Me₂ device where u', v' were 0.2008 and 0.4712, respectively.

ProDOT-Me₂ was prepared according to Scheme 1, which involved a transesterification between dimethoxythiophene (DMOT) and 2,2-dimethylpropane-1,3-diol catalyzed by *p*-toluenesulfonic acid. The synthesis of ProDOT-Ac is also a transesterification ring closure with DMOT and *p*-toluenesulfonic acid, but 1,1,1-tri(hydroxy-methyl)ethane is used as the diol to produce (3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methanol (ProDOT-OH). The synthesis of ProDOT-Ac includes one additional step of adding the acrylate group, which is obtained by deprotonation of the hydroxyl group on the ProDOT-OH monomer, followed by an addition of acryloyl chloride. Overall, this synthesis adds one additional high-yielding step with an average of 75% after recrystallization. The electropolymerization of the ProDOT-Ac electroactive

monomer onto the electrode is seen in Scheme 2, which is followed by UV curing of the device. During the UV curing of the device, not only does the gel cross-link with itself but also to the electrochromic polymer on the electrode and monomers still in the gel matrix (Scheme 2).

Response time for the ProDOT-AC devices was evaluated by optical spectroscopic measurements upon switching potential bias. Devices were switched between 2 and +2 V with an 8 s pulse width. The transmittance (%T) value was measured at 555 nm, the most sensitive wavelength to human eye,³⁰ and was monitored as a function of time during the redox cycling process. Herein, the switching speed of the devices (~ 5.8 cm² active area) was defined as the time required to achieve 95% of the full transmittance swing. From the %T versus time curve (Figure 4), the bleaching time is calculated to be 2 s and the coloring time is 1 s.

CONCLUSIONS

We have achieved long-term stability of in situ electrochromic devices, preparing samples that switched for over 10 000 cycles without any spotting defects and with minimal losses (3%) in photopic contrast. By cross-linking the backbone of the polymer to the gel matrix, the migration of monomers was inhibited by locking them within the solid-state gel matrix. This new procedure added only one additional step to the synthesis of the monomer, and the only modification to the device fabrication procedure was to polymerize electrochemically the monomer in the solution state. The photopic contrast of these devices was comparable with the more commonly used ProDOTs, such as 2,2-dimethyl-propylenedioxythiophene (ProDOT-Me₂), with the major difference being that the ProDOT-Ac devices lost 3% photopic contrast after 10 000 cycles, whereas the ProDOT-Me₂ devices lost 4% contrast after just 500 cycles. The colored state of the ProDOT-Ac devices was similar to the ProDOT-Me₂ devices, allowing them to be interchangeable from an electrochromic perspective. Most importantly, the oxidized states of the ProDOT-Ac devices were transparent, making these monomers capable of use in eyewear, windows, or any other application where a colorless bleached state is required. The one-step lamination procedure for making electrochromic devices allows open-air fabrication, fast assembly times, and lower waste than traditional methods for manufacturing ECDs.

ASSOCIATED CONTENT

Supporting Information

Spectra on ProDOT-Ac, cyclic voltammetry, and pictures of the cycling studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are thankful to Alphachromics, Inc. as well as the University of Connecticut for their support of this work.

ABBREVIATIONS

ECD, electrochromic device
ProDOT, 3,4-propylenedioxythiophene
ProDOT-Ac, 3,4-propylenedioxythiophene-acrylate
ProDOT-Me₂, 2,2-dimethyl-3,4-propylenedioxythiophene
LITRIF, lithium trifluoromethanesulfonate
ACN, acetonitrile
ITO, indium tin oxide
CP, conjugated polymer
OTE, optically transparent electrode

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