

# Highly Regiosymmetric Homopolymer Based on Dioxythiophene for Realizing Water-Processable Blue-to-Transmissive Electrochrome

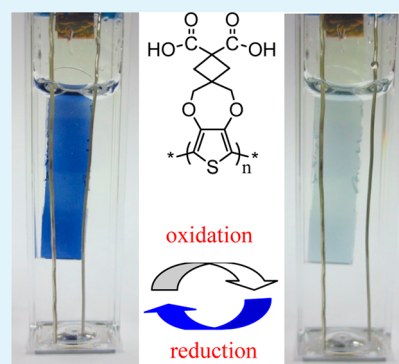
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## Supporting Information

**ABSTRACT:** A highly regiosymmetric homopolymer based on a diethyl malonate derivatized 3,4-propylenedioxythiophene (ProDOT) monomer was synthesized through FeCl<sub>3</sub> oxidative polymerization and postpolymerization functionalization to realize a water-processable blue-to-transmissive switching electrochromic polymer (WPECP-blue). As an electrochromic material, the polymer has a high electrochromic contrast  $\Delta T_{\max} = 56\%$  at 580 nm and a relatively fast switching speed  $t_{95} = 1.8$  s, and shows only contrast loss of 11% (from 56% to 45%) at square wave potential step of 5 s over 11 000 switching cycles, making it a desirable candidate for electrochromic applications such as windows and displays.



**KEYWORDS:** electrochromism, dioxythiophene, conjugated polymer, blue, transmissive

## INTRODUCTION

Electrochromic materials exhibit a change in transmittance and/or reflectance of electromagnetic radiation induced by an electrochemical oxidation–reduction reaction, and the phenomenon is called electrochromism.<sup>1–4</sup> A certain set of properties such as a desired absorption profile, an easily accessible redox process, and ease of processing are of essential importance for materials to serve as effective electrochromes.<sup>5</sup> In a comparison with their inorganic counterparts, conjugated polymers were proven to be the materials of choice due to their numerous advantages such as different colors obtained from the same material at different redox states (multichromism), the ease of band gap control with structure modification toward generating different colors, fast switching speed, and superior coloration efficiencies.<sup>6–8</sup>

More importantly, electrochromic polymers (ECPs) exhibiting a high degree of transparency in one of their redox states are of particular interest for electrochromic window or display applications where multiple chromophores can be incorporated and overlaid to achieve new colors.<sup>9</sup>

However, insolubility is the major limitation of conducting polymers. Synthesis of soluble conducting polymers enables direct application of these polymers to any substrate by conventional printing techniques such as inkjet printing or spray casting, etc.<sup>10</sup>

To allow materials to be incorporated into the large area device architecture of interest, great efforts have been made over the last 2 decades to synthesize novel, especially solution-processable, electrochromic polymers (SPECP) which can be

switched from colored neutral state to transmissive oxidized state.<sup>11–28</sup>

To date, most successful SPECPs, such as double substituted poly(3,4-propylenedioxythiophene) (PProDOT) at the 2-position of propylene bridge with alkyl/alkoxy groups developed by the Reynolds group<sup>16</sup> and benzotriazole or quinoxaline containing donor–acceptor type electrochromic polymers with alkyl/alkoxy groups on acceptor units synthesized by the Toppare group,<sup>17</sup> are capable of being processed in organic solvents such as toluene, chloroform, etc. That is a little unsatisfactory because volatile organic solvents are expensive and toxic, limiting the practical commercial utility of SPECP.

Thus, aqueous processability becomes one of the long-lived aspirations in the development of novel ECPs because the ability to spray-process ECPs from water is expected to minimize toxicity to operating staff, environmental pollution, and processing costs. This kind of effort was initiated by scientists at Bayer AG in Germany in the development of poly(3,4-ethylenedioxythiophene) (PEDOT). PEDOT is insoluble, yet it exhibits a very high conductivity, is almost transparent, and has a very high stability in the oxidized state. To resolve the solubility problem the polymerization of 3,4-ethylenedioxythiophene (EDOT) was carried out in an aqueous polyelectrolyte, poly(styrene sulfonic acid) (PSS),

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solution using  $\text{Na}_2\text{S}_2\text{O}_8$  as the oxidizing agent.<sup>29</sup> The reaction at room temperature results in a dark blue stable aqueous PEDOT/PSS dispersion with a net negative charge,<sup>30</sup> which is commercially available from Bayer AG under its trade name BAYTRON P (a famous star production in the field of organic electronics). After the remaining PEDOT/PSS film is dried, it is highly conducting, mechanically durable, and insoluble in any common solvents.<sup>29</sup> Recently, Gangopadhyay et al. have observed that PEDOT/PSS particles as a whole are enveloped in an outer PSS-water medium that is the key reason for the unique stability of this solution.<sup>31</sup>

Subsequently, single substituted PEDOT and PProDOT at the alkylene bridge with sulfonated group were synthesized by Reynolds<sup>32,33</sup> and Kumar,<sup>34</sup> and subjected to layer-by-layer depositions with nonelectrochromic polymer counterparts such as poly(allylamine hydrochloride) (PAH) perhaps due to the relatively low solubility in water.<sup>35</sup>

For large-area processing of a water-processable electrochromic polymer (WPECP), higher solubility in water should be achieved through introducing more than one hydrophilic pendant group such as ionic substituents. One very good paper on this subject has been published by Reynolds et al.<sup>35</sup> in which a side-chain defunctionalization approach was utilized to introduce two ionic carboxyl groups in one 3,4-propylenedioxythiophene (ProDOT) unit, yielding magenta-to-transmissive switching WPECP. The remaining purple hue was mainly due to the relatively smaller absorption of red light in the visible region. A simple homopolymer of ProDOT bearing alkyl ester side-chains is synthesized and subsequently hydrolyzed to get a polyionic salt that is spray-processable from water. Upon acidification the defunctionalized polymer recovers its electrochromic properties ( $\Delta T = 61.5\%$  at 575 nm in  $\text{KNO}_3/\text{H}_2\text{O}$  electrolyte with the optical density of the film  $A = 0.82$  au).<sup>35</sup>

As three additive primary colors red, green, and blue (RGB) are essential to constitute an important step forward for the use of conducting polymers in polymeric electrochromic devices,<sup>12</sup> using benzothiadiazole as the acceptor unit, a donor–acceptor type blue-to-transmissive WPECP with four ionic carboxyl groups in one ProDOT unit was synthesized through Stille polymerization by the Reynolds group and characterized ( $\Delta T = 52\%$  at 555 nm in  $\text{KNO}_3/\text{H}_2\text{O}$  electrolyte with the optical density of the film  $A = 1.04$  au).<sup>36</sup>

In general soluble dioxythiophene homopolymers do not yield blue polymers due to their lack of absorption in the far red.<sup>15</sup> For example, the first solution processable cathodically coloring electrochromic polymer, a purple tetradecyl substituted derivative of PEDOT, does not match the color of unsubstituted PEDOT. The regiorandom and atactic nature of the solubilizing side chains induces strong repulsion between repeats, reducing backbone planarity and limiting effective conjugation length in the neutral state. As a result the absorption is hypsochromically shifted when compared to that of the unsubstituted PEDOT, and the long wavelength absorption in the visible region is not enough to appear blue to the eye.<sup>15</sup>

Therefore, a suitable dioxythiophene monomer is appreciated which can be easily functionalized in simple reactions from commercially available starting materials and polymerized through simple homopolymer approach in a high-yielding reaction without using any comonomer and expensive catalysts.

In our recent study on colorimetric sensing of nonionic and cationic surfactants using a versatile anionic poly(3,4-propylenedioxythiophene) derivative WSPProDOT, we report

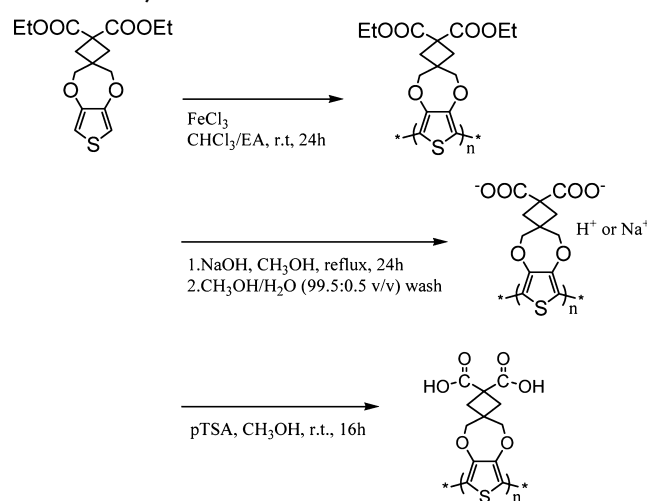
the synthesis of a novel dioxythiophene monomer based on ProDOT with diethyl malonate (DEM) pendant group and a cyclobutane spacer between ProDOT and DEM (ProDOTCB-DEM).<sup>37</sup> The solution color of WSPProDOT changes from purple to blue upon addition of nonionic surfactants and from purple to black for cationic surfactants due to the conformational change of WSPProDOT. This promotes the present study on the electrochromic application of ProDOTCBDEM. In our point the small cyclobutane moiety in ProDOTCBDEM could serve as a spacer between the solubilizing substituents and the polymer backbone, reducing the influence of side chains on the conjugation length of the main chain. Additionally the introduction of diethyl malonate as a pendant group of PProDOT makes the side chain more symmetric than other PProDOT derivatives because the C2 atom of malonate serves as a new symmetry center besides the C2 atom of propylene bridge of ProDOT.

In this paper, a highly regiosymmetric, water-processable, blue-to-transmissive switching electrochromic polymer was synthesized through simple  $\text{FeCl}_3$  oxidative homopolymerization and postpolymerization functionalization from PProDOTCBDEM to partially hydrolyzed PProDOTCB-salt and finally to PProDOTCB-acid. The electrochromic properties of the polymer were characterized in detail as presented below.

## RESULTS AND DISCUSSION

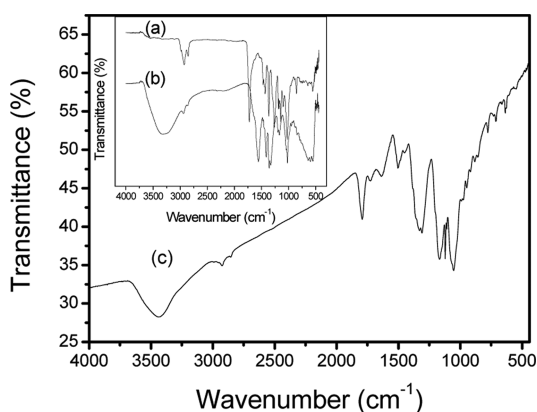
The synthetic route is depicted in Scheme 1. Synthesis of the monomer ProDOTCBDEM was reported in our previous

**Scheme 1. Synthesis of WPECP-blue**



work.<sup>37</sup> Dioxy-substituents are used for realization of a transmissive oxidized state and high redox stability because the electron donating character of dioxy-substituents stabilizes a closed-shell bipolaron structure in high p-doping levels.<sup>38</sup> The polymer PProDOTCBDEM was prepared by oxidative coupling of ProDOTCBDEM with excess anhydrous  $\text{FeCl}_3$  and transferred to water-soluble partially hydrolyzed PProDOTCB-salt by treatment with NaOH in methanol as reported by us previously.<sup>37</sup> It is worth noting that partially hydrolyzed PProDOTCB-salt has good solubility in water ( $>8$  mg/mL); thus, it can be spray-cast onto indium tin oxide (ITO) coated glass easily and demonstrates excellent film-forming characteristics.

Partially hydrolyzed PProDOTCB-salt was dissolved in water to a concentration of 8 mg/mL and then spray-cast onto ITO coated glass slides using high-pressure air (25 psi) with a conventional air-brush at room temperature until the desired absorption maximum of the film (2.3 cm × 0.7 cm) was achieved (between 0.5 and 1.4, corresponding to transmittance values from 32% to 4%). After that the film was forwardly acidified in 0.1 M solution of p-toluene sulfonic acid (pTSA) in methanol at room temperature for 16 h, and then washed with methanol. After being dried at room temperature the resulting polymer film is insoluble in any organic solvent or water, yielding PProDOTCB-acid. The postpolymerization functionalization process was monitored by Fourier transform infrared spectroscopy (FTIR), and the results are shown in Figure 1.



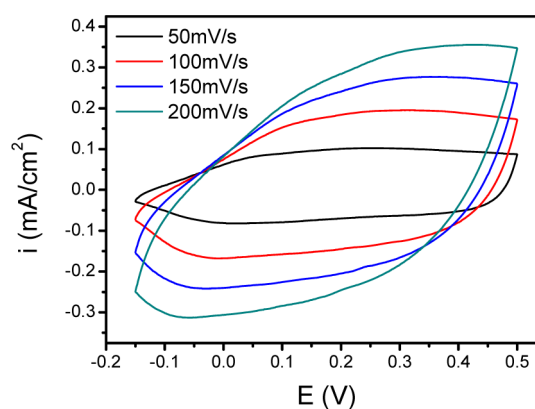
**Figure 1.** FTIR spectra of PProDOTCB-acid (c). The inset spectra of PProDOTCBDEM<sup>37</sup> (a) and partially hydrolyzed PProDOTCB-salt<sup>37</sup> (b) were also shown for comparison.

For comparison the IR spectra of PProDOTCBDEM and partially hydrolyzed PProDOTCB-salt were also shown.<sup>37</sup> The conversion of the polymer to its acid form is evidenced by the C=O band at 1790 cm<sup>-1</sup> and the -OH band at 3650–3000 cm<sup>-1</sup> in Figure 1c which are characteristics of the carboxylic acid.<sup>39</sup>

To allow direct comparison of the switching properties between polymer films, as suggested by Dyer,<sup>40</sup> we utilize the measurement of optical density rather than film thickness. This is because spray-cast polymer films are relatively rough with the measured thickness varying greatly across the film. Once the solvent was evaporated, the PProDOTCB-acid film (2.3 cm × 0.7 cm, *A* = 0.87 au) was subjected to cyclic voltammetry (CV) studies, under ambient conditions, to determine the redox potentials.

The electrochemical cycles were from -0.15 to 0.5 V with a Pt wire counter and Ag wire pseudoreference electrode in 0.1 M LiClO<sub>4</sub> (lithium perchlorate)/PC (propylene carbonate) contained in a cuvette. The Ag wire pseudoreference electrode was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc<sup>+</sup>) in the electrolyte (*E*<sub>1/2</sub>(Fc/Fc<sup>+</sup>) = +0.36 V versus Ag wire in 0.1 M LiClO<sub>4</sub>/PC). The potentials are reported versus Ag wire as has been suggested by Toppare.<sup>41</sup> PC is used as the solvent of the electrolyte because of its remarkable ability to dissolve and dissociate lithium salts and provide electrolytes with high ionic conductivity over a wide temperature range.<sup>42</sup>

The cyclic voltammetric results are shown in Figure 2. The polymer exhibits an oxidation peak potential of 0.30 V and a reduction peak potential of -0.05 V at the scan rate of 50 mV/



**Figure 2.** Cyclic voltammogram of PProDOTCB-acid film (2.3 cm × 0.7 cm, *A* = 0.87 au) at scan rates of 50, 100, 150, and 200 mV/s in 0.1 M LiClO<sub>4</sub>/PC.

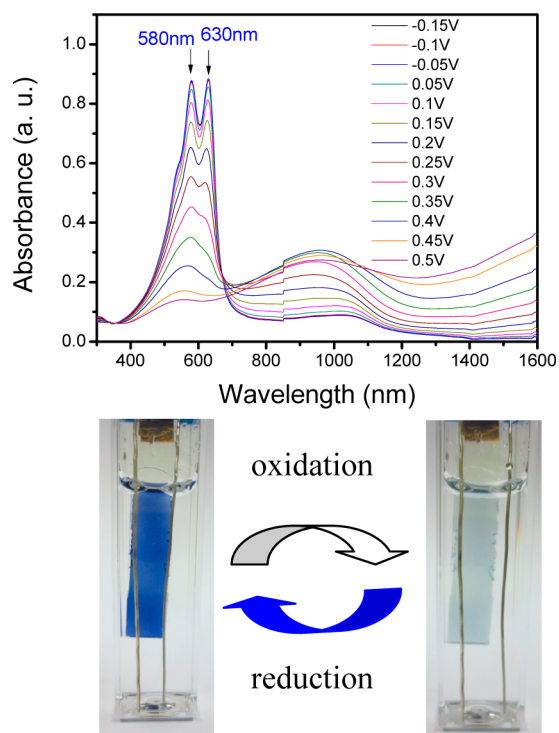
s. The scan rate dependence of the CV plots shows that the current varies linearly with scan rate, although there is a positive shift of the oxidation potential at faster scan rate, which indicates the presence of a well-adhered electroactive film; the polymer redox response is non-diffusion-limited up to 200 mV/s as suggested by Toppare et al.<sup>43</sup> The PProDOTCB-acid film (141 nm thickness) is rough and porous, and this is evidenced by the film surface roughness of 27 nm as shown in Figure S1 in Supporting Information. As Kumar<sup>34</sup> and Hammond<sup>44</sup> suggested, a surface-controlled non-diffusion-limited redox process corresponds to the open morphology of films and provides the faster inclusion and expulsion of ions during rapid electrochromic switching.

From an application point of view, the spectroelectrochemistry should be well-evidenced by the electronic absorption spectra under varied applied potentials. Therefore, UV-vis-NIR spectra of the PProDOTCB-acid film (*A* = 0.87 au) were recorded upon external bias. Figure 3 shows the spectroelectrochemical response in terms of absorbance as a function of wavelength as the potential was gradually increased from -0.15 to 0.5 V in a 0.1 M LiClO<sub>4</sub>/PC electrolyte-solvent couple with inset photographs of polymer coated ITO electrode in cuvette at the fully neutral state of the polymer (at the potential -0.15 V) and fully oxidized state (at the potential 0.5 V).

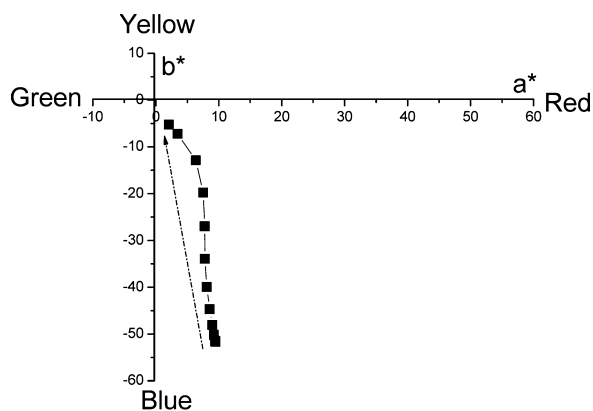
To report the polymer film colors quantitatively in a scientific manner, the color change of the polymer film during the redox process as a function of applied potentials was monitored by colorimetry study as shown in Figure 4. The color of a material is represented quantitatively using three attributes: *L*<sup>\*</sup> (brightness), and two color components *a*<sup>\*</sup> (the axis extends from -*a*<sup>\*</sup> (green) to +*a*<sup>\*</sup> (red)) and *b*<sup>\*</sup> (the axis extends from -*b*<sup>\*</sup> (blue) to +*b*<sup>\*</sup> (yellow)) as defined by Commission Internationale de l'Éclairage (CIE), allowing for effective comparison of the color of a material as it is switched in addition to comparison between various electrochromic materials.

As seen in Figures 3 and 4, at -0.15 V, bimodal absorption peaks where  $\lambda_{\max} = 580$  nm and  $\lambda_{\max}' = 630$  nm because of the  $\pi$ - $\pi^*$  transition are present in the bright blue neutral state (*L*<sup>\*</sup> = 50.1, *a*<sup>\*</sup> = 9.5, *b*<sup>\*</sup> = -51.8) with the optical density of the PProDOTCB-acid film *A* = 0.87 au, i.e., the transmittance *T* = 13.5%.

The introduction of diethyl manolate as a pendant group of the PProDOT makes the side chain more symmetric than other PProDOT derivatives because the C2 atom of malonate serves



**Figure 3.** Spectroelectrochemistry of PProDOTCB-acid film ( $A = 0.87$  au) at the potentials increasing in 50 mV steps from  $-0.15$  to  $0.5$  V in  $0.1$  M  $\text{LiClO}_4/\text{PC}$ .



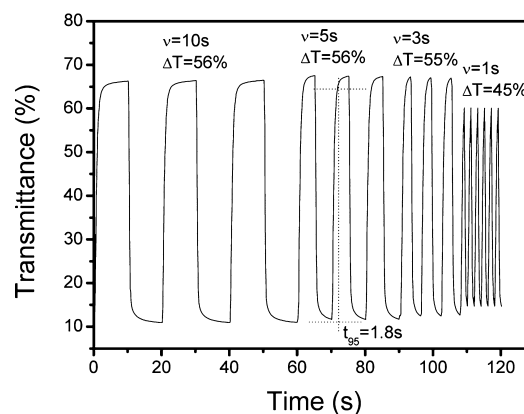
**Figure 4.** CIE 1976  $a^*b^*$  values of PProDOTCB-acid film ( $A = 0.87$  au) at the potentials increasing in 50 mV steps from  $-0.15$  to  $0.5$  V in  $0.1$  M  $\text{LiClO}_4/\text{PC}$ . The arrow shows the direction of increasing potential.

as a new symmetry center besides the C2 atom of propylene bridge of ProDOT. According to the suggestion of Cihaner,<sup>20</sup> this absorption splitting (bimodal absorption peaks) can be attributed to vibronic coupling concerning the formation of a highly regular polymer backbone containing symmetric alkyl chains. It is interesting that the pronounced bimodal peaks broaden the absorption at the longer wavelength 600–700 nm of the visible region; thus, more red light could be absorbed by this structure as compared with the structure reported by Reynolds group,<sup>35</sup> making the PProDOTCB-acid film show bright blue color. It is worth noting that the polymer was synthesized through  $\text{FeCl}_3$  oxidative homopolymerization which is a simple way to realize blue-to-transmissive ECP.

Upon stepwise oxidation, the intensity of the absorption due to the  $\pi-\pi^*$  transition reduces, and the polymer absorbs at longer wavelength in the near-IR region (about 950 nm) because of the polaronic transition. At higher oxidation levels, the bipolaron absorption ( $>1100$  nm) dominates the spectra. Upon full oxidation ( $L^* = 85.5$ ,  $a^* = -2.1$ ,  $b^* = -5.2$ ), the intensity of absorption at  $\lambda_{\text{max}} = 580$  nm is significantly reduced, showing highly transmissive oxidized state indicated by  $a^*$  and  $b^*$  values close to 0. The maximum transmittance change ( $\Delta T_{\text{max}}$ ) at 580 nm is 56%. It is worth noting that the residue absorption between 650 and 750 nm in the visible region makes the oxidized state of the polymer film exhibit a little transmissive sky blue.

Essential properties that govern an electrochromic's ability to be utilized in electrochromic devices involve the speed at which the polymer can be switched from one color state to another (as rapidly switching materials are desired), the electrochromic contrast, and the long-term switching stability.<sup>45,46</sup> The switching speed is typically represented as the time required for the polymer to reach 95% of full contrast when switched from neutral (highly absorptive) to fully oxidized (highly transmissive). The value of 95% is chosen as the human eye is relatively insensitive to the final 5% of a full optical contrast.<sup>40</sup>

Electrochromic switching studies were performed to monitor the transmittance as a function of time and to determine the switching times of the polymers at their  $\lambda_{\text{max}}$  by stepping the potentials repeatedly between their fully neutral and oxidized states. Figure 5 shows the change in transmittance at 580 nm of

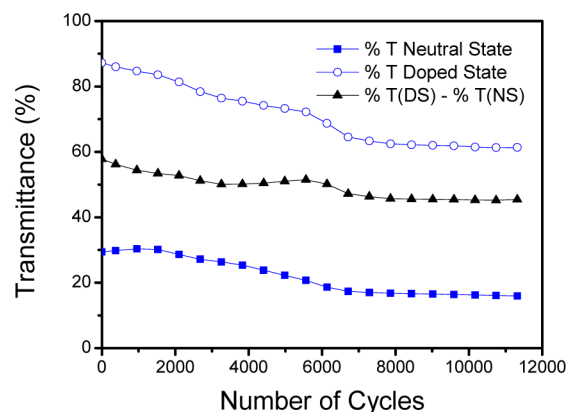


**Figure 5.** Square wave potential step absorptometry of PProDOTCB-acid film ( $A = 0.96$  au) at 580 nm,  $-0.15$  to  $0.5$  V in  $0.1$  M  $\text{LiClO}_4/\text{PC}$  with a Pt wire counter electrode, and Ag wire pseudoreference electrode.

a PProDOTCB-acid film ( $A = 0.96$  au), as a function of time, as potential square waves were applied from  $-0.15$  to  $0.5$  V. As can be seen in Figure 5, the film exhibits a relatively high full contrast  $\Delta T_{\text{max}} = 56\%$  at 580 nm, requiring 1.8 s to achieve 95% of a full switch in the oxidation process ( $t_{95} = 1.8$  s). The contrast remains 45% even at 1 s step.

The degradation of one of the redox states of an electrochromic material will result in rapid loss of electrochromic contrast. Therefore, an ECP must undergo a stable redox process for its electrochromic properties to be reproducible upon repeated switching (over 10 000 cycles).<sup>9</sup> In a long-term switching stability test, the square wave potential step was set as 5 s in which the transmittance change could reach the full contrast, and the polymer film shows only

contrast loss of 11% (from 56% to 45%) over 11 000 switching cycles as indicated in Figure 6, making it a desirable candidate for electrochromic applications such as windows and displays.



**Figure 6.** Long-term square wave potential step absorptometry of PProDOTCB-acid film ( $A = 0.53$  au) at 580 nm,  $-0.15$  to  $0.5$  V in  $0.1$  M  $\text{LiClO}_4/\text{PC}$  with a Pt wire counter electrode, and Ag wire pseudoreference electrode. The time each potential was held is 5 s.

## CONCLUSION

A highly regiosymmetric, water-processable, blue-to-transmissive switching electrochromic polymer was synthesized on the basis of a diethyl malonate derivatized ProDOT monomer through simple  $\text{FeCl}_3$  oxidative homopolymerization and postpolymerization functionalization from PProDOTCBDEM to partially hydrolyzed PProDOTCB-salt and finally to PProDOTCB-acid. The introduction of diethyl manolate as a pendant group of PProDOT makes the side chain more symmetric than those of the other PProDOT derivatives because the C2 atom of malonate serves as a new symmetry center besides the C2 atom of the propylene bridge of ProDOT. Water processability offers a green alternative to conventional organic solvent based processing methods that can facilitate the utilization of electrochromic polymer in industrial scale device applications. Its electrochromic potential as materials, switching between blue neutral state and a transparent regime, was investigated. The results showed that the polymer film has a high electrochromic contrast  $\Delta T_{\text{max}} = 56\%$  at 580 nm and relatively fast switching speed  $t_{95} = 1.8$  s, and shows only contrast loss of 11% (from 56% to 45%) at square wave potential step of 5 s over 11 000 switching cycles, making it a desirable candidate for large-area electrochromic applications such as windows and displays, which have been long-lived aspirations in our group.

Moreover, motivated by the high water solubility of partially hydrolyzed PProDOT-salt ( $>8$  mg/mL), the potential of the monomer ProDOTDEM as the donor unit in a donor-acceptor type electrochromic polymer is being studied for realizing a series of water-soluble electrochromic polymers with various colors of neutral states; therefore, a full color palette of WPECP could be achieved in the future.

## ASSOCIATED CONTENT

### Supporting Information

Experimental details and Figure S1. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01908.

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### Notes

The authors declare no competing financial interest.

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