Macromolecules **2009**, *42*, 135−140

Synthesis and Characterization of Regioregular Water-Soluble 3,4-Propylenedioxythiophene Derivative and Its Application in the Fabrication of High-Contrast Solid-State Electrochromic Devices

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Received July 28, 2008; Revised Manuscript Received November 10, 2008

ABSTRACT: Water-soluble sulfonated monomer based on 3,4-propylenedioxythiophene (ProDOT-sultone) was synthesized and characterized for the first time via the O-alkylation of the corresponding unreactive β,β-disubstituted hydroxyl group with propane sultone in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane (DABCO). This new monomer was oxidatively polymerized to produce regioregular water-soluble conjugated anionic polyelectrolyte, which was then used for the fabrication of solid-state electrochromic devices using the layer-by-layer (LbL) deposition method. These solid-state devices were found to exhibit better electrochromic properties in terms of color contrast, switching time, coloration efficiency (CE), surface control electroactivity, and conductivity in thin films compared with the corresponding water-soluble regiorandom 3,4-ethylenedioxythiophene (EDOT) derivative. For the 40 and 80 bilayer solid-state electrochromic devices, the electrochemical contrast was observed to be 31 and 40% at 570 nm with fast solid-state switching times of 100 and 220 ms, respectively, indicating faster movement of the ions in and out of the films. Furthermore, the CE was found to be as high as 250 cm^2/C for the 80 bilayer device and was independent of the device thickness, indicating the full accessibility of all of the ionic sites, even in thicker films. Four-point probe conductivity of the LbL and in situ conductivity of solution cast films were found to be in the range of 10^{-4} and 10^{-3} S/cm, respectively.

Introduction

Polymers based on 3,4-alkylenedioxythiophenes are an important class of conjugated polymers because of their widespread applications in the area of electrochromic devices, sensors, hole transport layers in OLEDs, and antistatic coatings.[1,2] These widespread applications of polymers based on 3,4-alkylenedioxythiophenes are possible because of their low oxidation potential, chemical stability in doped and undoped forms, high thermal stability, and high transparency in the doped state. Although these polymers do exhibit interesting properties, research progress in the area of structural variations for fine-tuning the properties or for studying the structure−property relationship is rather slow because of tedious multistep syntheses of the monomers. Therefore, it is the need of the hour to design a suitable monomer that can be easily functionalized without a protection/deprotection strategy in a single step in a high yielding reaction either in the monomer stage or after the polymerization. In this direction, hydroxymethyl-substituted 3,4-propylenedioxythiophene monomer, ProDOT-OH, provides an interesting alternative because a functional monomer such as this can be easily synthesized in a single step from commercially available starting materials. Mishra et al. were the first to report the successful functionalization and electropolymerization of ProDOT-OH, which opened up many opportunities in the area of functional conducting polymers.[3]

In this article we report for the first time the synthesis and characterization of a new water-soluble monomer and conjugated regioregular polymer based on sulfonated 3,4-propylenedioxythiophene (ProDOT-sultone). This polymer exhibits better electrochromic properties in terms of color contrast, switching time, coloration efficiency (CE), and surface control electroactivity and conductivity in thin films formed by the layer-by-layer (LbL) technique, compared with the corresponding water-soluble regiorandom 3,4-ethylenedioxythiophene (EDOT) derivative. The advantage of the water-soluble polymer is that it can be processed using a wide range of deposition techniques such as spin coating,[4] solution casting,[5] Langmuir−Blodgett (LB),[6] and LbL.[7] Furthermore, the introduction of the regioregular nature improves the material properties, as is observed for other regioregular polymers based on thiophene.[8,9]

Layer-by-layer deposition of polymeric thin films is a technique developed by Decher et al.[10,11] in which a substrate is dipped in alternating solutions of polycation and polyanion, which results in linear film growth with the ultimate thickness being controlled by the number of bilayers deposited. Zotti et al.[12] deposited the water-soluble polyelectrolyte polymers by using the LBL technique. The thin film deposition of polythiophene-based multilayers that were characterized in aqueous media was reported by Lukkari et al. as well.[7] Recently, Reynolds et. al and others[9,13] reported LbL deposition studies on a similar, but regiorandom polymer based on 3,4-ethylenedioxythiophene (PEDOT-sultone) for electrochromic devices and also as hole transport layers in OLEDs. We feel that the device characteristics and the polymer properties can be significantly improved by the design of a corresponding regioregular water-soluble polymer. Therefore, in this article, we report the synthesis of a new monomer, ProDOT-sultone, and its polymer, PProDOT-sultone, by the use of an oxidative polymerization route. Studies on electrochemical and spectroelectrochemical properties and conductivity measurements of the films were carried out by depositing the films by using the solution cast

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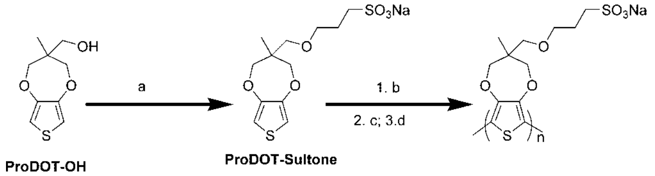
10.1021/ma801708d CCC: $40.75

Scheme 1. Synthesis of Monomer and Polymer



a) NaH, THF, DABCO, propane sultone, room temp. 24h; b) $FeCl_3$, $CHCl_3$, room temp.24h; c) hydrazine hydrate, 24h d) 1% methanolic solution of NaOH, 24h

method and the LbL method. The films formed by the LbL method were characterized in organic and aqueous media, whereas the solution cast film was characterized in organic media because of the solubility of the polymer in aqueous media. This polymer shows unusual acid doping phenomena similar to those reported by the Reynolds group.[14] The films formed by the LbL method using polyallylamine hydrochloride (PAH) as the cationic polyelectrolyte were used in the fabrication of solid-state electrochromic devices, which exhibit fast switching times. The synthesis and characterization of this new water-soluble regioregular polymer along with the studies on solid-sate electrochromic devices are reported here in this article.

Results and Discussion

ProDOT-sultone monomer was synthesized by O-alkylation of ProDOT-OH with propane sultone in the presence of DABCO as a catalyst, as shown in Scheme 1. The monomer was fully characterized for its molecular structure by the use of NMR, FTIR, and HR-MS. ProDOT-OH was first reported by Kros et al.[15] in 2002 and caught the attention of various researchers around the globe because this was one of the easiest ways to introduce hydroxyl functionality as a side chain in the class of monomers based on 3,4-alkylenedioxythiophenes. Interestingly, it turned out that this excitement was short-lived because most of the efforts to functionalize this hydroxyl group with various alkylating agents such as alkyl halides, allyl halides, propargyl halides, propane sultone, and so on were futile as a result of the β,β-disubstituted nature of the hydroxyl group. However, limited success in functionalizing this type of β,β-disubstituted hydroxyl group via benzylation was reported by our group[3] and via alkylation by Reynolds and coworkers.[16] It should be noted here that although the benzylation does occur in most of the solvents, alkylation only occurs in DMF solvent. This was confirmed by the fact that alkylation in solvents other than DMF was unsuccessful. Furthermore, the use of other alkylating agents such as allyl or propargyl halides or propane sultone in DMF as solvents was also unsuccessful. In our continued efforts to discover suitable reaction conditions for the functionalization of this β,β-disubstituted hydroxyl group of ProDOT-OH, we were pleasantly surprised to find that the presence of a catalytic amount of DABCO or 1,8-diazabicycloundec-7-ene (DBU) resulted in the successful O-alkylation of ProDOT-OH with various alkylating agents such as allyl halides, propargyl halides, propane sultone, and so on. However, the exact role of DABCO or DBU as a catalyst is not very clear in this stage, and work is in progress to understand its role. It is sufficient to say here that the use of DABCO or DBU is essential for the success of the O-alkylation of the hydroxyl group of ProDOT-OH and it opens up various avenues for the simple one-step syntheses of functional monomers based on ProDOT-OH. It should also be mentioned here that the success of DABCO or DBU as a catalyst is independent of the solvent used as well as the alkylating agent used.

The monomer ProDOT-sultone was then oxidatively polymerized using iron(III) chloride in chloroform by stirring at room temperature. It should be mentioned here that the monomer was insoluble in chloroform but the oxidizing agent was soluble and hence the polymerization effectively occurred in the solid state. The polymerization proceeded in the usual fashion wherein a color change from light yellow to light green to dark blue with time was observed. We isolated the polymer by precipitating the reaction mixture in methanol, followed by stirring with hydrazine hydrate to undope the polymer and finally with 1% methanolic solution of sodium hydroxide to convert counterions back to sodium. The resulting undoped polymer was isolated as a dark-blue powder and was found to be insoluble in common organic solvents but was soluble in water. The chemical polymerization of ProDOT-sultone is supported by an observed red shift of the $\pi-\pi^*$ transition upon polymerization.

This polymer showed an absorption at λ_{max} of 554 nm (2.2 eV) with a band gap of 1.78 eV. In the FTIR spectra, the band at 3097 cm^{-1}, which is characteristic of the ProDOT C−H (end group) vibration of the ProDOT-sultone, disappears completely upon polymerization, indicating the successful polymerization. The presence of absorption due to the symmetric and asymmetric S=O stretching mode at 1045 and 1190 cm^{-1} in both the monomer and the polymer is consistent with the proposed structures and stabilities of the pendant chains under the polymerization conditions.[8] The polymeric nature of the material is also evident from the low optical band gap (1.78 eV) compared with that of the corresponding monomer. The MALDI-TOFMS analyses confirmed the presence of chains of molecular weights of up to 6500 $g \cdot mol^{-1}$, which is in no way limiting or average because of the inability of longer chains with a sulfonate group to be volatized.[8] Surprisingly, all of the attempts to produce well-defined solution ^1H NMR with reasonable resolution were not successful because of the poor resolution of the spectrum in D_2O, which is in agreement with other cases of conjugated polyelectrolytes.[8] The thermogravimetric analysis of the polymer PProDOT-sultone was carried out under nitrogen at a heating rate of 10 °C/min, which showed that the polymer remains stable up to 290 °C after which rapid weight loss is observed because of the degradation of the polymer. It was interesting that a solution of the polymer in water would result in precipitation upon storage. Initially, we thought that the polymer had a low shelf life in water, which results in decomposition upon storage. However, careful examination of the polymer structure revealed that the precipitation from the water solution results from the ionic cross-linking of the backbone upon partial self-doping due to the sulfonated side chains. The backbone forms cationic species upon self-doping, which then forms ionic cross-links with the anionic sulfonate group in the side chain. This ionic cross-linking was found to be reversible, as confirmed by the redissolution of the precipitated polymer upon the addition of a few drops of any reducing agent such as hydrazine hydrate.[17] This phenomenon of reversible cross-linking due to self-doping has a technological advantage in self- and reversible curing of the thin films because the doped thin films were found to be insoluble in water, although water was used as the solvent to cast thin films.[12]

Electrochemical Studies on PProDOT-Sultone. The scan rate dependence of the polymer thin films deposited using the LbL method was studied in both aqueous and organic media by recording the cyclic voltammogram. In organic media, 0.1 M $LiClO_4$/ACN, the thin films showed a well-defined oxidation peak, whereas a broad peak was obtained when TBAP was used as an electrolyte. This is in agreement with the data reported by Reynolds and coworkers in the case of regiorandom PEDOT-sultone.[8] However, in aqueous media, 0.1 M $LiClO_4$ in water, the thin films exhibited a sharp oxidation peak centered around 0 mV at a scan rate of 50 mV/s. The sharp oxidation peak changes to a broad peak when the electrolyte is switched to 0.1 M $NaClO_4$. This is attributed to the size of the cation, which

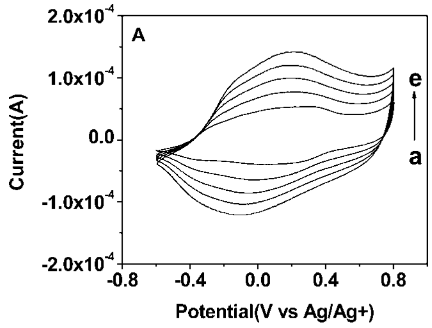


Figure 1. Cyclic voltammogram of chemically synthesized PProDOT-sultone deposited on ITO-coated glass at scan rates of (a) 5, (b) 10, (c) 15, (d) 20, and (e) 25 mV/s in 0.1 M LiClO_4/ACN (5% water).

plays an important role in the redox behavior of the polymer because of its inclusion and expulsion during potential cycling.[18] The scan-rate dependence of polymer deposited by the LbL method in 0.1 M LiClO_4/water suggests that the polymer redox response is non-diffusion-limited up to 1000 mV/s as the current varies linearly with scan rate, although there is an anodic shift of oxidation peak at higher scan rate. Also, as Hammond and coworkers[19] explained, a surface-controlled non-diffusion-limited redox process corresponds to the open morphology of the multilayers and provides the faster movement of the ions in and out of the film that is required for rapid electrochromic switching. However, a surface-controlled redox process also lowers the contrast because the whole film thickness is not utilized. In this work, the films are formed to obtain a good combination of high contrast and fast switching speed to avoid the tradeoff between these two values. This is one of the most significant advantages of the LbL film formation technique: the film thickness and morphology can be easily controlled by a slight variation in the ionic strength of the polyelectrolytes through the salt concentration and pHs of the deposition solutions.[20] The cathodic shift of the peak potential in the cyclic voltammogram comes from the internal resistance of the bulk film[21] and primarily arises from the slow electron transfer from the ITO electrode to the PProDOT-sultone via the resistive inactive polycation, PAH.

To study the effect of thin film formation on electrochemical properties, studies were carried out on thin films formed by drop casting from solution. For this purpose, 10 mg of the polymer was dissolved in 1 mL of water and was used for drop casting the thin film on ITO-coated glass electrodes. These thin films were then studied for their electrochemical properties in 0.1 M LiClO_4/ACN (5% water) (Figure 1) as the films used to fall out from the electrode in pure water during electrochemical scanning. Well-defined redox peaks were observed up to a scan rate of 25 mV/s, which then broadens when the scan rates are increased to 200 mV/s. The oxidation peak potential of the polymer was centered at 0.1 V versus Ag/Ag^+ at 25 mV/s. It is interesting that the LbL films of PProDOT-sultone/PAH deposited from water were found to be electroactive in both organic and aqueous media; the films deposited by the solution cast method were electroactive in only an organic medium. Furthermore, the porous nature of the well-adhered film to the electrode surface deposited by the LbL method allowed for greater cation mobility.[22]

For spectroelectrochemistry, a thin film of the polymer was drop casted (from a 10 mg/mL solution of polymer in water) on ITO-coated glass, and the spectra of the polymer were recorded at different applied potentials in 0.1 M LiClO_4/ACN, as shown in Figure 2. At −1 V, the polymer showed a $\lambda_{\max}$ of 557 nm because of the $\pi-\pi^*$ transition. Upon stepwise oxidation, the absorption due to the $\pi-\pi^*$ transition decreases, and the polymer absorbs at longer wavelength in the near-IR region (900 nm) because of the polaronic transitions. At higher oxidation levels, the bipolaron band absorption (>1100 nm) dominates the spectra, whereas $\pi-\pi^*$ and polaronic transitions remain relatively constant. In the neutral state, PProDOT-sultone absorbs throughout almost the entire visible region with deep-purple-blue color. An optical band gap (E_g) of 1.78 eV was calculated from the onset of the $\pi-\pi^*$ transition. The polymer shows a well-defined isosbestic point around 667 nm, which implies that only one kind of chromophoric species (PProDOT-sultone) is involved.

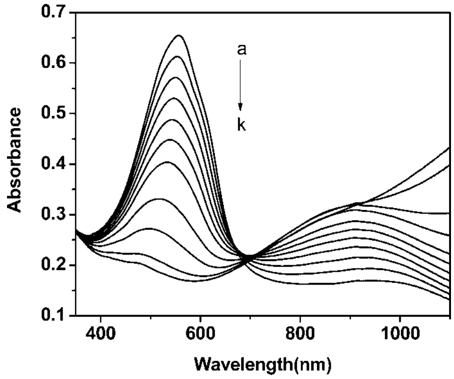


Figure 2. Spectroelectrochemistry of PProDOT-sultone casted on ITO-coated glass electrode in 0.1 M TBAP/ACN at (a) −1.0, (b) 0.1, (c) 0, (d) 0.1, (e) 0.15, (f) 0.2, (g) 0.3, (h) 0.4, (i) 0.6, (j) 0.8, and (k) 1.0 V.

The spectroelectrochemistry of 40 and 80 LbL films was carried out in 0.1 M TBAP/ACN at different applied potential following the procedure mentioned above. The multilayered films were first reduced with hydrazine hydrate, followed by repeated washing with acetonitrile before being subjected to spectroelectrochemical studies. The spectroelectrochemistry of the LbL films is essentially identical to that of the solution cast films. In the case of the LbL films, the polymer also has a maximum absorption at 557 nm due to the $\pi-\pi^*$ transition at −1.0 V. Upon stepwise oxidation of the film, the absorption due to the $\pi-\pi^*$ transition decreases with an increase in charge carrier absorbance bands at longer wavelengths centered around 900 nm. The films deposited by the LbL method also undergo a transition to the oxidized state through an isosbestic point upon oxidation like the solution-casted film.

Fabrication and transmission spectra measurements of the symmetrical solid-state devices made up of conducting electrochromic polymer (PEDOT) have been previously shown by Mecerreyes et al.[23] In our case, this symmetrical configuration utilizes PAH/PProDOT-sultone LbL films as electroactive layers on each of the two ITO-coated substrates, similar to our recent work for PEDOT.[24] In brief, a potential of 1.5 V is applied to the two PProDOT-sultone layers, and the device changes color from light blue to dark purple-blue. The change in color occurs because of the neutral state of only one of the PProDOT-sultone layers, whereas the other PProDOT-sultone layer remains oxidized and does not contribute to the color change. The device goes back to the original light-blue color once the potential is switched back to 0 V, and it shows no degradation or memory effect. An important thing to note here is that PProDOT-sultone, being a conjugated polymer, can form symmetrical devices and hence does not need a reduction partner for switching. This also results in fast switching of the symmetrical solid-state devices as compared with nonsymmetrical solid-state devices in which both cathodically and andoically coloring material is required for device switching.

Electrochromic switching speed measurements of PProDOT-sultone were performed in both liquid electrolyte solution and the solid state. For electrochromic switching studies in solution,

Table 1. Physical Properties of the PProDOT-Sultone Films Deposited Using Solution Cast Method and LbL Method

polymer PProDOT-sultone		λ_{max} (nm)	optical band gap (eV)	contrast (%ΔT)	switching time (s)
in water		554	1.78		
solution cast thin films		557	1.78	40	1.2
LbL thin films	40 bilayers	557	1.78	40	1.2
	80 bilayers	557	1.78	46	1.1
solid-sate devices	40 bilayers	570		31	0.1
	80 bilayers	570		42	0.22

polymer films were deposited by both solution cast method and LbL method on ITO-coated glass, and each polymeric film was stepped between its reduced (−1.0 V) and oxidized (+1.0 V) state in 0.1 M TBAP/ACN. As the films were switched, the %T at λ_{max} (557 nm) was monitored as a function of time. The contrast is given as the difference between %T in the reduced and oxidized states and is reported as %ΔT. The film deposited by solution cast method gives an electrochromic contrast of ~40% with a switching time of 1.2 s. Films with 40 and 80 bilayers give an electrochromic contrast of 40 and 46%, respectively, under static conditions (Table 1). The switching time was calculated from the time taken to reach 95% of the full contrast while switching the polymer from its fully oxidized to fully reduced state. Surprisingly, the film with 80 bilayers (Figure 3) demonstrated equally faster switching time (1.1 s) as compared to the 40 bilayer film (1.2 s). This indicates the easy movement of ions in and out of the film, which is independent of film thickness. This is in sharp contrast with earlier reports on solid-sate electrochromic devices wherein switching times were found to be inversely related to film thickness.[14,25] The composite CEs for 40 and 80 bilayer films were found to be 165 and 250 mC/cm^2, which is very high compared with other EC materials deposited by the LbL method.[7,8,26−29]

Switching Studies of Solid-State Devices. The transmission spectra of solid-state PAH/PProDOT-sultone devices made from two 20 bilayer and 40 bilayer PAH/PProDOT films are presented in Figure 4 at a constant potential of 0 or 1.5 V. Upon switching the device between 0 and 1.5 V, the 40 bilayer (2 films of 20 bilayers on ITO sandwiched together) and 80 bilayer (2 films of 40 bilayers on ITO sandwiched together) devices (Figure 5) showed a maximum contrast of 31 and 42%, respectively, at 570 nm. The change in transmittance is much higher than that of devices with a similar number of bilayers reported by Hammond and coworkers[30] for PEDOT and polyaniline (PANI) solid-state devices. The spectra in the solid-state are similar to the spectra in the liquid electrolyte solution for 40 bilayers of PAH/PProDOT-sultone.

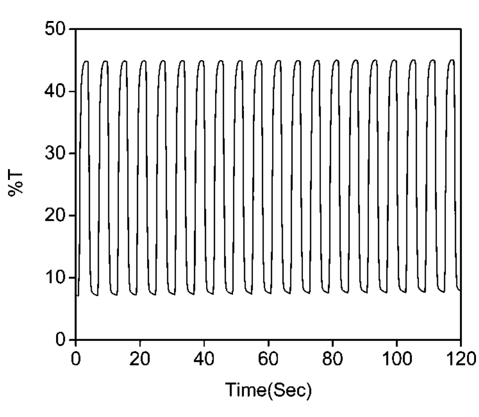


Figure 3. Optical switching studies for 80 bilayer LbL film as monitored by the %T at 557 nm when it was stepped between its reduced (−1.0 V) and oxidized (1.0 V) states.

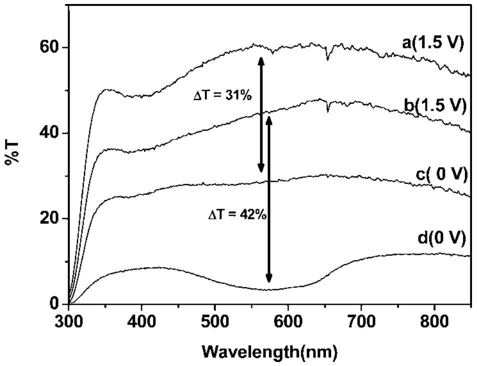


Figure 4. Transmission spectra of solid-state device of 40 (curves a and c) and 80 (curves b and d) bilayer PAH/PProDOT films at 0 (a and b) and 1.5 V (c and d).

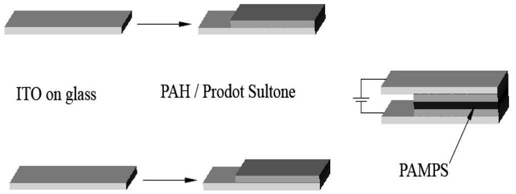


Figure 5. Schematic of a solid-state device.

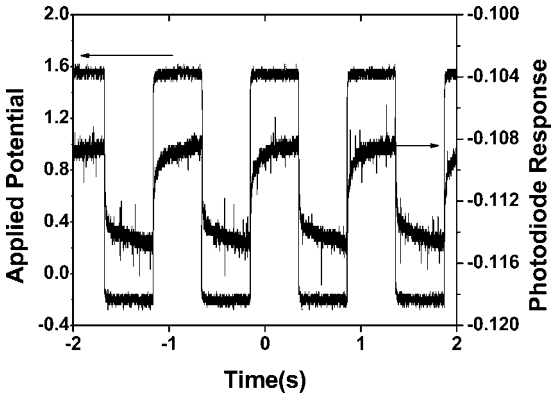


Figure 6. Photodiode signal versus time with square wave voltage applied for a 40 bilayer device with 1 cm^2 area.

The switching speed of the 40 bilayer devices was monitored over time with a He−Ne (633 nm) laser and photodiode as the square wave voltage (~1.5 V) was applied to the solid-state device (Figure 6). First, the switching speed curve shows the complete switching cycle, whereas the other two are the blow ups for coloration and decoloration time. (See the Supporting Information.) The device has coloration and decoloration times of 100 and 50 ms, respectively. It is interesting that this is one of the fastest switching speeds reported to date for solid-state electrochromic devices deposited using the LbL technique.[19] Therefore, polymers based on ProDOT-sultone have the potential to be used as valuable electrochromic materials for next generation flat-panel display prototype devices with high contrast and long-term stability.[31−33]

Conclusions

For the first time, we have successfully shown the synthesis methodology for the O-alkylation of the unreactive β,β-disubstituted hydroxyl group of ProDOT-OH using DABCO or DBU as a catalyst. This synthesis methodology is independent of the alkylating agent as well as the solvent used and hence opens up a synthesis route for the design and syntheses of functional conducting polymers based on 3,4-propylenedioxythiophene. The use of propane sultone as an alkylating agent resulted in the syntheses of water-soluble sulfonated monomer and regioregular polymer based on 3,4-propylenedioxythiophene. It was interesting to note the improvements in the electrochemical properties due to the regioregular nature of the polymer based on PProDOT-sultone as compared with that of regiorandom PEDOT-sultone. The fast switching speed of the solid-state devices, fabricated by LbL deposition, makes PProDOT-sultone a potential candidate for ultrafast flat-panel displays. Because of the flexibility of the LbL assembly method, it should be noted that it has the potential to be used for the fabrication of multihue electrochromic devices by combining with cationic electrochromic materials (such as polyviologen, PANI, etc.). The combination of PProDOT-sultone with other water-soluble cationic polyelectrolytes (both electrochromic and inactive) is currently in progress, and the detailed study of their effect on film thickness, contrast, and switching speed will be presented in our future publications.

Experimental Section

Tetrabutylammonium perchlorate (TBAP) and lithium perchlorate ($LiClO_4$) were purchased from Fluka and used without further purification. The monomer PProDOT-sultone was synthesized from ProDOT-OH. PAH with M_w ca. 70 000 was purchased from Aldrich and used without further purification; all of the other chemicals were of reagent grade and were without further purification. HPLC grade acetonitrile was used for electrochemical studies and was dried over calcium hydride prior to use. Indium doped tin oxide (ITO)-coated glass slides with dimensions of 3 × 1 in^2 (12Ω) were obtained from Delta Technologies. Solid-state devices were fabricated by pressure laminating LbL-coated ITO electrodes with the help of binder clips for 20 min and then sealing the ends with the epoxy so that the transparent conducting gel poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) (15 wt % in H_2O, Sigma-Aldrich) did not degrade from overexposure to air; the overall device configuration is shown in the schematic. Fabrication of the symmetrical solid-state devices made up of conducting electrochromic polymer has been previously shown by Mecerreyes et al.,[18] and in our case, this symmetrical configuration utilizes PAH/PProDOT-sultone LbL films that are similar to the electroactive layers on each of the two ITO-coated substrates.

All electrochemical experiments were carried out in a EG&G PAR model 362 potentiostat/galvanostat or a PINE AFCBP1 bipotentiostat controlled by Pine Chem software using a three-electrode cell with Ag/Ag$^+$(0.01 M $AgNO_3$/ACN) as the reference electrode and a platinum flag as the counter electrode. For spectroelectrochemistry experiments, indium-doped ITO-coated glass slides from Delta Technologies were used as the working electrode, and a silver wire was used as a quasi-reference electrode. For in situ conductance measurements, Ag/Ag$^+$ was used as the reference electrode. UV−vis spectra were recorded on either a Perkin-Elmer Lambda 25 or a Filmetrics UV−vis spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a VXR 400 NMR spectrometer. The chemical shifts are referenced to TMS. ES-MS analysis was carried out on a Waters Q Tof micro-YA-105 instrument. Thermogravimetric analysis (TGA) of the polymer PProDOT-sultone was carried out under a nitrogen atmosphere using Metler-Toledo TGA/SDTA 851 equipment.

Synthesis of (Sodium 3-((3-Methyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-3-yl)methoxy)propane-1-sulfonate.(ProDOT-Sultone). Sodium hydride (228 mg, 9.5 mmol) was added to a two-necked round-bottomed flask with 20 mL of dry THF under an argon atmosphere. To this suspension was added ProDOT-OH (2 g, 10 mmol) dropwise, followed by 1 mol % of DABCO. The mixture was allowed to stir for 20 min. A THF solution of propane sultone (1.15 g, 9.5 mmol in 10 mL of THF) was added dropwise to this suspension while the temperature was maintained at below 10 °C using an ice bath. After the addition was over, the reaction mixture was allowed to stir at room temperature for 15 h, and then the reaction mixture was quenched by the addition of methanol. The precipitated product was collected by centrifuge, washed several times with chloroform and ethyl acetate, and vacuum dried to produce a pale-white solid.

Yield: 356 mg (91%). ^{1}H NMR ($CDCl_3$, δ): 0.94 (s, 3H), 1.99−2.04 (m, 2H), 2.95−3.00 (m, 2H), 3.60 (s, 2H), 3.61−3.66 (m, 2H), 3.76 (d, J = 12 Hz, 2H), 4.03 (d, J = 12 Hz, 2H), 6.69 (s, 2H). ^{13}C NMR ($CDCl_3$): 16.13, 24.22, 42.63, 47.91, 68.69, 72.71, 76.82, 106.79, 148.62. FTIR (NaCl, cm^{-1}): 3103, 2963, 2869, 1641, 1558, 1486, 1449, 1380, 1186, 1110, 1046, 1019, 968, 850, 775, 612. ES-MS: 367.13 (M + Na)$^+$. HR-MS: 345.04 (M + 1)$^+$.

Polymerization of ProDOT-Sultone. For oxidative chemical polymerization, ProDOT-sultone (1 g, 2.90 mmol) was suspended in 100 mL of chloroform in the presence of 3.3 equiv of iron(III) chloride, and the reaction mixture was stirred at room temperature under an argon atmosphere for 24 h. The color of the reaction mixture changed to blue after 2 h, indicating the polymer formation. After 24 h, the polymer was isolated by centrifugation after the addition of methanol to the reaction mixture. The polymer was first washed with methanol and then stirred with a methanolic solution of hydrazine hydrate for 24 h, followed by 1% methanolic solution of sodium hydroxide to produce the final undoped polymer as dark-blue powder with sodium as counterions in 65% yield.

Layer-by-Layer Deposition of PProDOT-Sultone/PAH Films. The polymer films were formed by the alternate deposition of ITO glass slide (R_s= 10−12 Ω, Delta Technologies) first in a 10 mM PAH solution and then in a 2 mM solution of PProDOT-sultone for 6 min, followed by rigorous rinsing in Milli-Q water for 2 min after every step. LBL film assembly was done in an automated slide stainer (Nanostrata). ITO substrates were cleaned first by acetone and then by Milli-Q to ensure a strong LbL template. The ITO slides were dipped in 1 M NaOH for 15 min to provide enough negative charge so that the first layer of PAH deposited well on the ITO slides. ITO slides of a desired design were etched by masking the nonetched area by 3M electrical tape, followed by deposition in a 1:1 mixture of water and HCl for 1 h. Next, the electrical tape was removed, and the slides were cleaned with acetone and then ultrasonicated in the base solution (70/20/10% $H_2O/NH_4OH/H_2O_2$) for 30 min prior to use.

Film Thickness Measurement. Film thickness measurements were performed on a J. A. Woollam VB-2000 ellipsometer and were also confirmed by a LEO 1550 field emission scanning electron microscope (FE-SEM) at an accelerating voltage of a 5 KV profilometer (AMBIOS TECH XP-2). Although the measured values agree with all three techniques with a variation of ±5% of overall film thickness, the presented results are of the ellipsometry measurements. (See the Supporting Information.) The thickness of 40 and 80 bilayer films of PAH/PProDOT-sultone is approximately 145 and 300 nm, respectively. The Lorentz oscillator best-fit model is used to calculate the thickness of the LbL films. Overall, the film is quite smooth and homogeneous; the film roughness after various bilayer measurements is estimated to be typically <5% of the film thickness.

Acknowledgment. We acknowledge the Department of Information Technology (DIT) and Department of Science and Technology (DST) India for financial support. We also thank Professor A. Q. Contractor for allowing us to use his electrochemical facilities. R.S., S.P.M., and J.S. thank CSIR India for Senior Research Fellowships. H.M.Y. acknowledges support from the Sweet Briar College Faculty Fellowship.

Supporting Information Available: Solution spectra of reduced polymer in water and after the addition of APS, FTIR spectra of the monomer ProDOT-S and the polymer PProDOT-S, increase in total film thickness of PAH/PProDOT-sultone film with an increase in the number of bilayers, cyclic voltammogram of chemically synthesized PProDOT-S deposited on ITO-coated glass, scan rate dependence of a 40 LbL film, in situ conductance of PProDOT-sultone, and coloration and decoloration of the solid-state devices. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA801708D