

# Optical, electrochemical and morphological investigations of poly(3,4-propylenedioxythiophene)–sultone (PProDOT–S) thin films

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**Abstract.** In this paper, we have carried out thin film characterization of poly(3,4-propylenedioxythiophene)–sultone (PProDOT–S), a derivative of electrochromic poly(3,4-propylenedioxythiophene) (PProDOT). PProDOT–S was deposited onto transparent conducting oxide coated glass substrates by solution casting method. Single wavelength spectrophotometry is used to monitor the switching speed and contrast ratio at maximum wavelength ( $\lambda_{\max}$ ). The percentage transmittance at the  $\lambda_{\max}$  of the neutral polymer is monitored as a function of time when the polymer film is repeatedly switched. This experiment gives a quantitative measure of the speed with which a film is able to switch between the two states i.e. the coloured and the bleached states. PProDOT–S films were switched at a voltage of 1.9 V with a switching speed of 2 s at  $\lambda_{\max}$  of 565 nm and showed a contrast of  $\sim 37\%$ . Cyclic voltammetry performed at different scan rates have shown the characteristic anodic and cathodic peaks. The structural investigations of PProDOT–S films by IR spectra were in good agreement with previously reported results. Raman spectra of PProDOT–S showed a strong Raman peak at  $1509\text{ cm}^{-1}$  and a weak peak at  $1410\text{ cm}^{-1}$  due to the C = C asymmetric and symmetric stretching vibrations of thiophene rings. The morphological investigations carried out by using scanning electron microscope (SEM) of polymer films have shown that these polymers are found to be arranged in dense packed clusters with non-uniform distribution having an average width and length of 95 nm and 160 nm, respectively.

**Keywords.** Electrochromic materials (EC); PProDOT–S thin films; cyclic voltammetry; spectroelectrochemistry.

## 1. Introduction

Devices using polymer systems are gaining potential attention due to increasing need of low cost large-scale electronic devices. Conducting polymers have been investigated for their semiconducting and electrochemical properties, which have a number of device applications such as light emitting diodes, electrochromics, photovoltaic, sensors and field effect transistors. Electrochromics are the materials which change their colour as a function of applied potential (Monk *et al* 1995; Mortimer 1999; Rosseinsky and Mortimer 2001). Many organic and inorganic materials have been studied for their electrochromic property (Habib and Murphy 1992; Granquist 2000; Granquist *et al* 2003). Electrochromic materials are used extensively in the fabrication of different types of polymer electronics devices like light emitting diodes, electrochromic windows (Sindhu *et al* 2006; Liu *et al* 2008; Vacca *et al* 2008), photovoltaic cells, field-effect transistors (FETs) (Burroughes *et al* 1995; Yu *et al* 1995; Woo *et al* 2005; Shao 2011) etc. Electrochromic materials undergo a

change in their transmittance of heat and visible light when a small current or voltage is applied through them. This property of electrochromism of conducting polymers makes them important and attractive for smart windows applications. The term ‘smart window’ was coined by Svensson and Granqvist (1984). In this case, one of the limit redox states (oxidized/neutral) of the materials is transparent to visible light (clear state) while the other is absorbent (dark state). The absorbance can be tuned under proper electrochemical control, to any of intermediate values (Sindhu *et al* 2006; Liu *et al* 2008; Vacca *et al* 2008). The development of these electrochromic devices has been optimized by two main challenges: contrast and maximum lifetime. Significant advancements have been made to increase the lifetime of devices, including the use of ionic liquids.

Among all conductive polymers, polythiophene and its derivatives have observed to be good candidates owing to good environmental stability. However, due to the  $\alpha$ – $\beta$  coupling between thiophene rings during polymerization and high oxidation potential of monomer leads to polymer with poor applications. In order to overcome this problem, an alkenedioxy bridge between the 3rd and 4th positions create good electron density to the aromatic ring and reduce the high oxidation potential of the monomer (Mishra *et al* 2004). The optical properties of the polymers can be improved by

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modifying the polymer structure. The structural modifications of polymer backbone to enhance the optical properties have been systematically studied by Welsh *et al* (1999a,b). The optical properties which can be increased by increasing the ring size of the alkenedioxy group as well as substituting the bulky group on the ring has been reported previously (Krishnamoorthy *et al* 2001). Sarada *et al* (2004) synthesized a series of mono- and di-substituted 3,4-alkenedioxythiophene derivatives with good optical properties and high electrical conductivity.

In this article, we report the study of optical, electrochemical and morphological properties of poly (3,4-propylenedioxythiophene) – sultone (PProDOT-S) thin films prepared by solution cast techniques.

## 2. Experimental

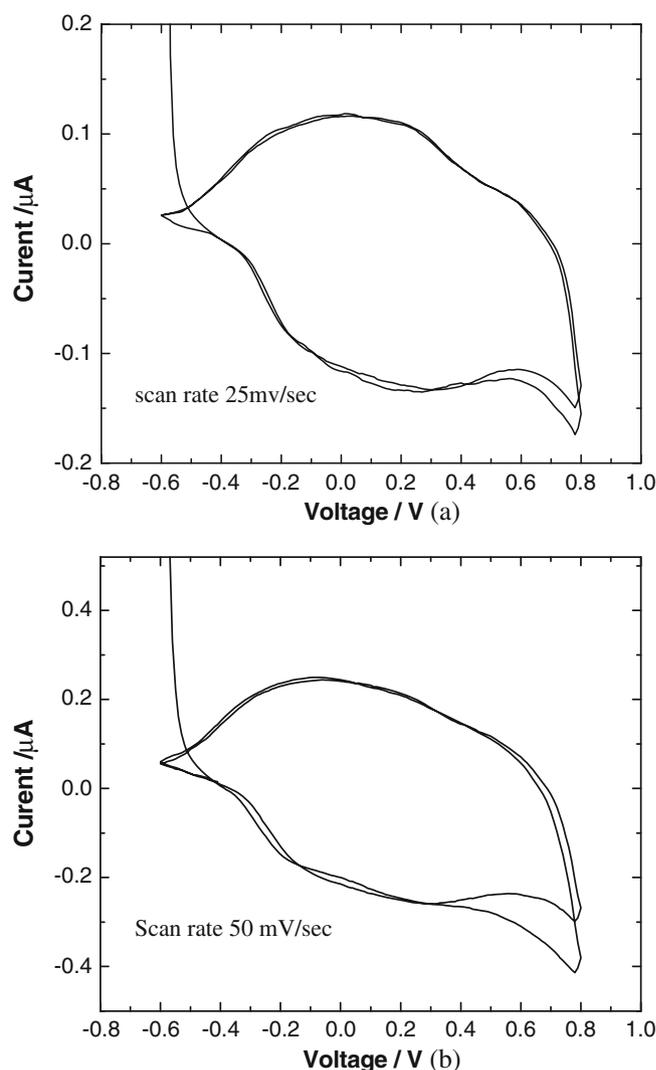
The monomer, sulphonated 3, 4-propylene dioxythiophene (ProDOT-S), was polymerized by chemical oxidative polymerization method (Jain *et al* 2009). Thin films of PProDOT-S were obtained by solution casting method onto transparent conducting oxide coated glass substrates (Ikenoue *et al* 1990). Indium tin oxide (ITO) coated glass substrates were purchased from Delta Technologies, USA. These substrates were cleaned using propanol and distilled water, followed by ultrasonification in acetone for 10 min. These cleaned substrates were dried in room temperature with air blower/nitrogen purging. The PProDOT-S solution of  $\sim 0.2$  ml was taken in a syringe and dispersed over the substrates in the form of droplets of  $\sim 1$  mm in diameter. The sizes of these drops were increased until a uniform distribution of solution was formed on the entire substrate. These solution cast films were dried for 10–15 min. Then the additional solution from the substrates was soaked up by using the same syringe. The thickness of the prepared PProDOT-S film was  $\sim 12$   $\mu\text{m}$ . These thin films were used for morphological followed by electrochemical studies.

The electrochemical studies of the PProDOT-S films were carried out by using CH Instrument (Model CHI6005D) at scan rates of 25 and 50 mV/s in 0.1 M TBAP in ACN electrolyte solution. The studies were done using PProDOT-S film coated on ITO/glass substrate as working electrode, platinum wire as counter electrode and Ag/Ag<sup>+</sup> as reference electrode.

Absorbance and optical switching studies for PProDOT-S films were carried out in 0.1 M TBAP in ACN electrolyte solution using Ocean Optics HR 4000 Spectrophotometer. Fourier-transform infrared spectroscopy (FTIR) studies of the prepared PProDOT-S films were carried out using OCUS FTIR spectrophotometer in the spectral range of 400 nm to 4000  $\text{cm}^{-1}$ . The Raman spectroscopy studies of the PProDOT-S films were performed by using Elmer Instruments, UK, at room temperature. The morphological studies were accomplished by scanning electron spectroscopy, Quanta Scanning Electron Microscope.

## 3. Results and discussion

The cyclic voltammetric studies performed at different scan rates revealed several interesting features. The cyclic voltammogram recorded for PProDOT-S with scan rates of 25 and 50 mV/s are shown in figure 1 (a and b). It is evident from figure 1a that a broad peak is seen at  $-0.41$  V at a scan rate of 25 mV/s, while the peak gets shifted to  $-0.47$  V at a scan rate of 50 mV/s (figure 1b) in 0.1 M TBAP in ACN electrolyte solution. The appearance of the broad peak during forward and reverse cycling indicates that the polymer is redox active with a large capacitive component. The charge of anodic and cathodic scans is found to be same. The occurrence of anodic as well as cathodic peaks in these scans shows that this polymerization reaction is reversible in nature, in the case of PProDOT-S films. Furthermore, it is found that an increase in the scan rates and monomer concentration have resulted



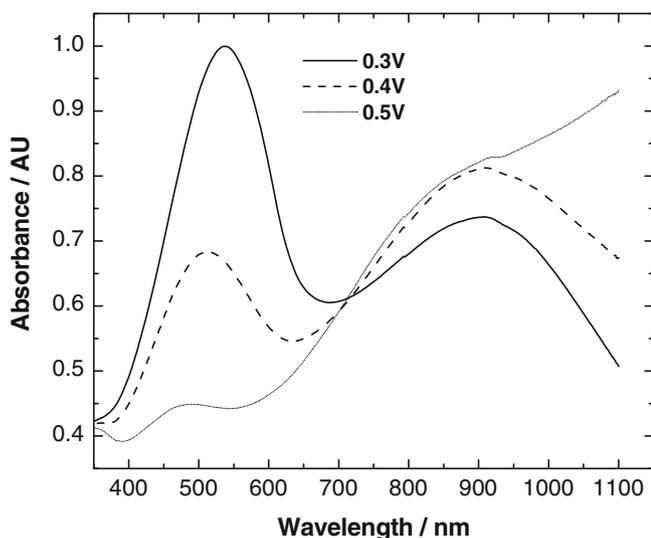
**Figure 1.** (a) Cyclic voltammogram recorded for PProDOT-S at scan rate 25 mV/s and (b) typical cyclic voltammogram recorded for PProDOT-S at a scan rate of 50 mV/s.

in increase in the electrode current and oxidation overpotential.

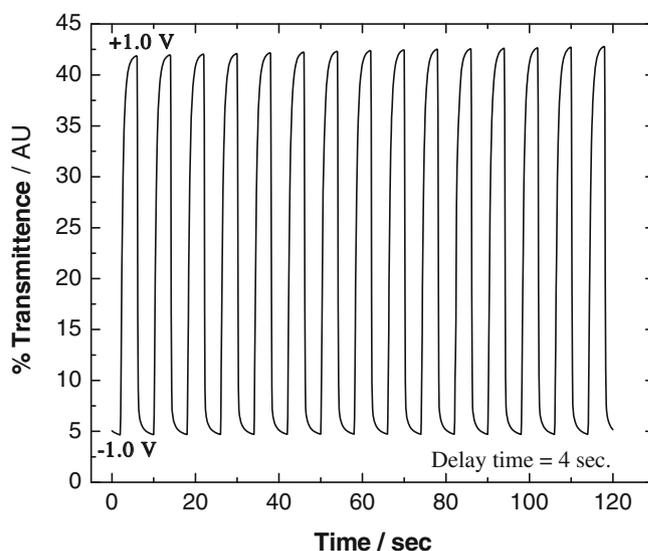
The optical spectra recorded for PProDOT-S thin film performed with ITO-coated glass as a working electrode in 0.1 M solution of TBAP in ACN is shown in figure 2. The peak was observed at 538 nm corresponding to an energy value of 2.30 eV at 0.3 V due to the vibronic coupling. The colour change from deep blue to opaque blue (Sindhu *et al* 2006) seen in the PProDOT-S is unique and can be attributed to either due to alkylene or restricting the extent of  $\pi$ -overlap along the polymer backbone. Similarly peaks were observed at 513 nm and 485 nm (energy values, 2.42 eV and 2.56 eV) at 0.4 V and 0.5 V potential, respectively. These peaks shift to lower wavelength (red shift) with an increase in applied potential.

Lack of fine structure may originate from inefficient  $\pi$ -stacking of the twisted backbone and may also explain the sharp, well defined polymer redox process. Upon stepwise oxidation of the polymer, absorbance of the  $\pi$  to  $\pi^*$  transition decreases and increases the polaron peaks at a higher wavelength region. At 0.5 V, the absorbance of  $\pi$  to  $\pi^*$  decreased, and the polymer turned from transparent to deep blue. The contrast calculated from the difference in percentage transmittance (% $T$ ) between the completely reduced and oxidized states was  $\sim 37\%$  (figure 3). While in the bleached state, lower potential of 0.3 V exhibits lower absorbance of 70% at 902 nm (1.37 eV) as compared to higher potential of 0.5 V, larger absorbance of 80% at 920 nm (1.35 eV), which shows that bleached state of PProDOT-S also blue shifted with applied potential. The colour contrast of PProDOT-S thin films may be found to be lower than the previous reports; however, we observed that this is the highest value reported to date with simple solution cast method.

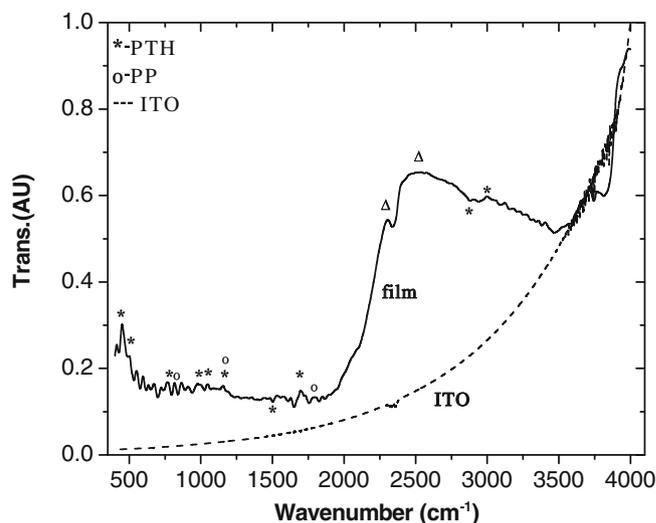
For optical switching studies, the polymer films were synthesized on ITO coated glass substrate by solution casting



**Figure 2.** Spectroelectrochemical studies of PProDOT-S polymer thin films on ITO coated glass substrate at various applied potentials.



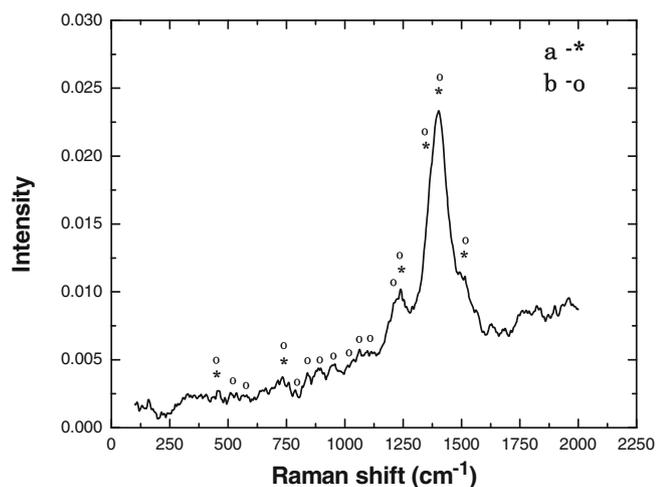
**Figure 3.** Optical switching studies for PProDOT-S film stepped between its reduced (1.0 V) and oxidized state (+1.0 V) at  $\lambda_{\max} = 565$  nm.



**Figure 4.** Typical FTIR studies for PProDOT-S film monitored by transmission mode. Solid line indicates the recorded spectra of PProDOT-S film and dotted line shows spectra of bare ITO substrate, respectively (PP-polypropylene, PTH-polythiophene).

method. The optical switching study of the PProDOT-S film is shown in figure 3. PProDOT-S films were switched from an oxidized state to reduced state by applying a potential of 1.0 V to  $-1.0$  V and recorded the % transmittance at  $\lambda_{\max}$ , 565 nm, as a function of time. Contrast ratio can be given by the difference between the reduced and oxidized states, which is represented by  $\Delta\% T$ . Switched data of films that produces the maximum percentage in  $\Delta\% T$  is as shown in figure 3. In this particular experiment, optical switching time response for film with a delay time of 4 s have been recorded.

Stability studies also have been performed for PProDOT-S film to determine contrast as a function of time. PProDOT-S films have accomplished stability studies with continuous switching in solution from +1.0 V to -1.0 V at room temperature. This polymeric film did not reveal any significant change in contrast, even after 5000 cycles. This indicates that our PProDOT-S films are highly stable even after long

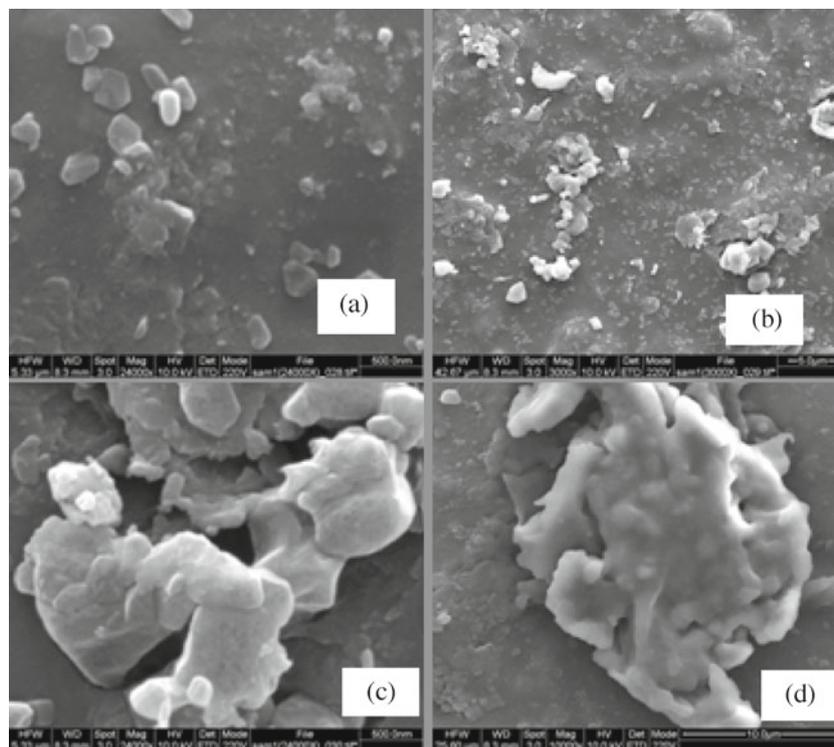


**Figure 5.** Raman spectra of PProDOT-S film deposited on ITO/glass substrate at room temperature.

cycles. So deposited PProDOT-S films have better characteristics in terms of contrast, low switching voltage for its use in high quality electrochromic device.

The structural studies of PProDOT-S films were analysed before cyclic voltammetry to avoid loss of sample. FTIR spectroscopy shown in figure 4, solid and dotted lines indicate the spectra obtained for PProDOT-S film and bare ITO coated glass substrate, respectively. The vibrations at  $3014\text{ cm}^{-1}$  and  $2871\text{ cm}^{-1}$  corresponds to the  $\text{C-H}_\alpha$  stretching and aliphatic methylene stretching of polythiophene rings. The small peaks at  $1680\text{ cm}^{-1}$ ,  $1642\text{ cm}^{-1}$  and  $1492\text{ cm}^{-1}$  represents the  $\text{C=O}$  stretching vibrations and aromatic  $\text{C=C}$  stretching in benzene ring of polythiophene (Metin *et al* 2005). Three small peaks at  $1157\text{ cm}^{-1}$ ,  $1049\text{ cm}^{-1}$  and  $980\text{ cm}^{-1}$  represent the bipolaron formation, quinoid character and co-existence of the charge carriers in the benzene ring of polythiophene (Varis *et al* 2006). The peaks at  $773\text{ cm}^{-1}$  and  $434\text{ cm}^{-1}$  indicate the  $\text{C-S}$  stretching and formation of polaronic charges in thiophene which are in good agreement with the previously reported results (Aysegul *et al* 2007).

While comparing the recorded data with polypropylene, small shoulders at about  $1720\text{ cm}^{-1}$ ,  $1750\text{ cm}^{-1}$  and  $1780\text{ cm}^{-1}$  indicate the simultaneous formation of ketone, ester and lactone groups. We also notice absorption peaks at about  $800\text{ cm}^{-1}$ ,  $1150\text{ cm}^{-1}$  and  $1260\text{ cm}^{-1}$  which corresponds to  $(-\text{CH}=\text{CH}-)$  and (ether-linkage). But these weak absorptions were difficult to determine due to overlap with



**Figure 6.** SEM image of PProDOT-S films: (a) view of single particles rich regions, (b) formation of clusters, (c) zoom view of clusters and (d) zoom view of single crystal only.

the isotactic PP bands as shown in Gosse *et al* (1992). The peaks at 1300–1900  $\text{cm}^{-1}$  and 2600–4000  $\text{cm}^{-1}$  revealed the formation of carbonyl and hydroxyl containing species (Kitching and Donald 1998). Also the IR range from 3400–4000  $\text{cm}^{-1}$  indicates the exponential rise due to ITO substrate. The two new peaks observed at 2280–2510  $\text{cm}^{-1}$  may be due to the di-oxy functional group in PProDOT-S.

The PProDOT-S films were analysed by Raman spectroscopy as shown in figure 5. The position of the Raman bands which are associated with the existence of the  $\pi$ -bonding system (C=C stretching) usually depends on the excitation wavelengths. Vibrations from the segments involving smaller conjugation length will be enhanced by shorter excitation lines ( $\lambda_{\text{exc}} \sim 450$  nm), whereas those from longer conjugated segments will be in resonance with the red ( $\lambda_{\text{exc}} \sim 676.4$  nm) or near infrared radiation ( $\lambda_{\text{exc}} \sim 1064$  nm) excitation wavelengths. Interestingly,  $\lambda_{\text{exc}} \sim 450$  nm, we have taken for resonance with short chains. We observed a distribution of the conjugation length with two bands located at 1509 and 1410  $\text{cm}^{-1}$  of two strong bands due to the C=C asymmetric and symmetric stretching vibrations. These corresponded to the thiophene rings at the end and in the middle of the chains, respectively. The band in the vicinity of 1350, 1239  $\text{cm}^{-1}$  and 1208  $\text{cm}^{-1}$  are due to the inter ring stretching of polymer chains. Two bands at lower wave numbers like 720  $\text{cm}^{-1}$  and 450  $\text{cm}^{-1}$  are due to C-S-C deformation i.e. symmetric  $C_{\alpha}=C_{\beta}$  stretching deformation in the planar mode of vibration of thiophene.

In oxyethylene mode, broad bands at around 1510, 1410, 1345  $\text{cm}^{-1}$  and 1234  $\text{cm}^{-1}$  have been observed which may exist due to  $\text{CH}_2$  bending in the molecular chains. Three small peaks at 1110, 1069 and 1065  $\text{cm}^{-1}$  were observed due to C-C stretching and C-O stretching in the polythiophene. Oxyethylene ring deformation or breathing was also observed at 954, 825  $\text{cm}^{-1}$  and 797  $\text{cm}^{-1}$ . Peaks at 576, 523  $\text{cm}^{-1}$  and 440  $\text{cm}^{-1}$  due to C-S-C ring deformation occurred in PProDOT-S. It is observed that the spectrum of PEDOT obtained by chemical oxidative polymerization reveals good agreement with observed spectrum of PProDOT-S film.

The morphological studies of the PProDOT-S film were done by scanning electron microscopy. Figure 6 shows (a) view of the single particles-rich regions, (b) formation of clusters, (c) zoom view of the clusters, (d) zoom view of single crystal only at different thicknesses. The observed morphology comprised of non-uniform distribution of polymeric molecules along with clusters. A collection of dense packing with average width and length of  $\sim 95$  nm and  $\sim 160$  nm, respectively was observed. The above-described morphological illustration reveals for a strong ordering of the polymeric bundles parallel to the substrate. While the zoomed view of cluster morphology indicating like a cauliflower with many recesses in it are as reported by Xiao *et al* (2004). This apparently increases surface area of the electrode. As from these SEM images, it is also clear that the surface morphology depends on the surface area of the conducting polymer deposited on the sites and the cluster formation

could be controlled by varying the thickness of PProDOT-S films.

#### 4. Conclusions

We studied the structural, optical and electrochemical characterization of thin films of PProDOT-S deposited onto ITO coated glass substrates.

The cyclic voltammetric studies of PProDOT-S thin films at a scan rate of 25 mV/s results in anodic onset at  $-0.41$  V, indicating cathodically colouring of PProDOT-S film. Moreover, simultaneous occurrence of anodic and cathodic peaks confirm the reversible nature of the material, PProDOT-S, in the thin film form. The spectro-electrochemical studies of the films reveal red shift in coloured state and blue shift in bleached state with increase in potential. Optical switching studies showed  $\sim 37\%$  contrast. The switching studies for over 5000 cycles showed good stability of the PProDOT-S thin film.

The FT-IR and Raman spectra of PProDOT-S films revealed that the polymerization of monomer leads to the formation of polymer PProDOT-S. The morphological studies of polymer films show that the polymers are arranged like clusters of dense packing of non-uniform polymer materials with average width and length of 95 nm and 160 nm, respectively.

The detailed investigation of these electrochromic polymer thin films forms the basis for the fabrication of electrochromic windows.

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