

Influence of Surfactants on the Electrochromic Behavior of Poly (3,4-ethylenedioxythiophene)

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ABSTRACT: Electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) was carried out in presence of two different surfactants, sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) in aqueous medium. The cyclic voltammograms of the polymers exhibited well-defined redox peaks at $E_{ox} = 140$ mV, $E_{red} = 360$, and -180 mV for PEDOT/SDS and $E_{ox} = 360$ mV, $E_{red} = 540$, -140 mV for PEDOT/CTAB. The electroactive polymer showed good adherence. The spectroelectrochemical studies were carried out on ITO glass plate at various applied potentials. The oxidized PEDOT/CTAB was opaque blue in color and the reduced form was transparent yellow in color. Electrochromic parameters such as electrochromic efficiency (or coloration efficiency), stability

(or cycle life), and optical contrast (or write-erase efficiency) and stability were determined and presented. The *in situ* conductance was measured at applied potentials ranging from -0.6 V to 0.7 V. The polymer was resistive initially at -0.6 V (7.5×10^{-5} S cm⁻¹) and reached maximum conductance of 1.7×10^{-3} S cm⁻¹ at 0.5 V in presence of SDS. The polymer formed with CTAB exhibited high resistive behavior. The surface morphology characteristics were also studied. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3285–3291, 2007

Key words: electrochromism; 3,4-ethylenedioxythiophene; sodium dodecyl sulfate; cetyl trimethyl ammonium bromide; spectroelectrochemistry

INTRODUCTION

Conducting polymers have been used as materials in electrochromic windows,¹ lightweight batteries, LEDs, sensors, and actuators.² Among the conducting polymers, polyaniline and polypyrrole can be easily synthesized by chemical and electrochemical polymerizations. However, the poor stability of these polymers is a hindrance for potential applications.^{3,4} Polythiophene is a relatively stable conducting polymer but the synthesis by electrochemical initiation is very difficult because of the high oxidation potential of thiophene.⁵ This problem has been overcome by the introduction of 3,4-ethylenedioxythiophene. This monomer is oxidized at 1.1 V versus Ag/Ag⁺, which is 1 V less than that of thiophene.⁶ The polymer is found to be very stable in oxidized and reduced states, switches between opaque blue to transparent blue colors in 2.2 s. The band gap of the polymer is 1.6 eV.⁷ These interesting properties attracted the attention of researchers from academic and industrial labs that resulted in application of this polymer in various devices.⁸ Bayer AG prepared a water dispersion of PEDOT using poly (styrene sulfonate) as

a stabilizer. This dispersion has been used to make pixels using plastic sheet as support.⁹ Most of the research on PEDOT is focused on improving the electrochromic properties. Reynolds and coworkers synthesized various derivatives of EDOT and improved the contrast of the polymer to 78% in case of dimethyl substituted poly(3,4-propylenedioxythiophene).¹⁰ Very recently, Kumar and coworkers synthesized and characterized a dibenzyl substituted poly(3,4-propylenedioxythiophene) that exhibited the highest contrast (89%) reported till date.¹¹ Reynolds and coworkers designed and fabricated various electrochromic devices using PEDOT and its derivatives as electrochromic material. From their experiments they found that a complementary electrochromic polymer is necessary as counter electrode to improve the device stability. Poly(3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-*b*]dioxepine) (PProDOT-Me₂) possessed the higher coloration efficiency (375 cm² C⁻¹) compared with poly(3,4-ethylenedioxythiophene) (PEDOT) (183 cm² C⁻¹) and poly(3,4-propylenedioxythiophene) (PProDOT) (285 cm² C⁻¹), because of a combination of larger changes in optical density at λ_{max} and higher doping levels as reported by Reynolds and coworkers.¹² Composite coloration efficiency values were found up to 1365 cm² C⁻¹; this was considerably larger than the values obtained from previously studied alkylenedioxythiophene-based polymers (~ 375 cm² C⁻¹).¹³ The polymerization of

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thiophene monomers was carried out in aqueous media by Sakmeche et al.¹⁴ using anionic micelles. The anionic micelles appear to shift the oxidation of the monomer to lower the potentials.^{15,16} Addition of anionic surfactants^{17,18} nonionic surfactants¹⁹ and certain organic compounds²⁰ led to the formation of monomer micro emulsions. PEDOT nanoparticles with enhanced conductivity and processability were produced by polymerization in surfactant micellar solution.²¹ Sadki and Chevrot copolymerized EDOT with sodium dodecylsulfate (SDS) in aqueous micelles solution.²² We have already reported the electrochemical synthesis and characterization of novel electrochromic poly (3,4-ethylenedioxythiophene-*co*-Diclofenac) with surfactants.²³ Polyaniline was used as counter electrode to improve the device stability but the response time was improved significantly when a copolymer of carbazole and EDOT was used.^{24–26} Using this configuration, IR electrochromic devices were fabricated by the same group and others.^{27,28} Thus the above researches conclude that a counter electrode polymer, which has a higher band gap, is a must for better device fabrication. Till date the counter electrode polymers were synthesized using tedious synthetic procedure.

Herein, we report on the synthesis and characterization of dual electrochromic PEDOT, which was synthesized from EDOT in presence of a cationic surfactant²⁹ cetyl trimethyl ammonium bromide (CTAB). Interestingly, the polymer synthesized in the presence of CTAB was transparent yellow in the reduced state and opaque blue in the oxidized state. This is an exact mimic of the polymer based on bisEDOT-carbazole.

EXPERIMENTAL

Materials and methods

EG and G M273A Potentiostat/Galvonostat (Princeton Applied Research Corp.) was employed for electropolymerisation studies. UV-VIS spectrophotometer Jasco-V-530 was used for spectroelectrochemical studies. The solutions of 0.01M EDOT, 0.01M SDS, 0.1M KCl, and 0.001M CTAB were prepared in deionized water. A single compartment three-electrode system was used for cyclic voltammetric studies. Glassy carbon electrode was used as working electrode, platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode. *In situ* spectroelectrochemistry was studied using ITO-coated glass slides as working electrode. *In situ* conductance was measured using Pine AFRDE 4 bipotentiostat. The polymer film surface morphology was studied by computer-controlled Hitachi S3000 H SEM.

RESULTS AND DISCUSSION

Cyclic voltammetric behaviors

Growth of PEDOT (Fig. 1) was studied in aqueous 0.1M KCl media in the potential range from -600 to 1300 mV at a scan rate of 50 mV s⁻¹ using cyclic voltammetry. The monomer underwent oxidation and resulted in a peak around 1240 mV in the first cycle. The peak current decreased in the subsequent cycles and the intermediates, diradical dication/bipolaron produced in the oxidation of monomer reacted with another molecule of monomer and produced radical cation polarons. These radical cations underwent redox reaction much easily around 320 mV and the polymer formed was deposited on the electrode surface. Because of this redox behavior, an anodic peak around 320 mV and cathodic peak around 680 mV were observed in the third cycle. The increase in the peak currents seen in the consecutive cycles suggested the polymer growth on the electrode surface. Similar results had been reported earlier.²² A blue color PEDOT was seen on the electrode after the completion of 15 cycles. As the number of cycle was progressing, the redox process might be facilitated and the polymer growth was noticed. Hence the anodic peak was shifted to more anodic potential and cathodic peak to more cathodic potential. This indicates quasireversible to reversible redox process of polymer growth. The formed polymer was washed with deionized water and cycled between -600 and 800 mV in the monomer free electrolyte. As the scan rate increased the peak current increased suggesting adherent film (Fig. 2). The correlation between the anodic peak current and scan rate exhibited linearity ($i_{pa} = 0.3225 v - 0.474$) with good correlation, $r^2 = 0.999$ (Fig. 3).

0.01M EDOT monomer was electropolymerised in presence of anionic¹⁷ surfactant of 0.01M SDS and 0.1M KCl using 0.01M solution of monomer in aqueous

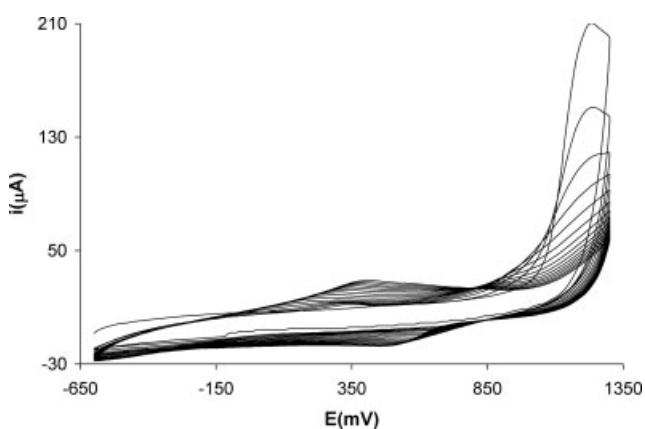


Figure 1 Cyclic voltammogram of 0.01M EDOT in aqueous 0.1M KCl on GCE scan rate 50 mV/s

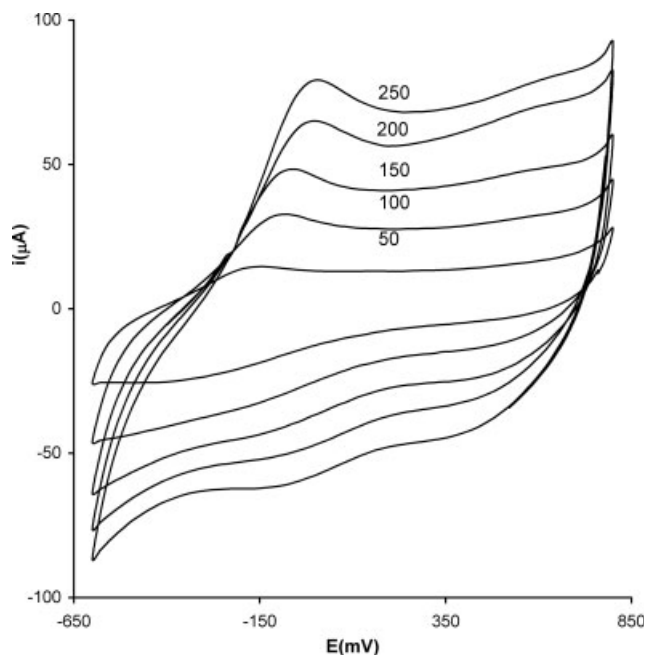


Figure 2 Cyclic voltammogram of PEDOT/KCl film in 0.1M KCl scan rate variation from 50 to 250 mV/s

medium by cycling the potential at 50 mV s⁻¹ between -0.6 and 1.3 V versus SCE. The monomer oxidation peak starts at 720 mV and peaks at 1120 mV (Fig. 4). Well-developed polymer redox waves were observed in the consecutive cycles indicating the formation of an electroactive polymer film on the electrode surface. The polymer oxidation was observed at 140 mV in the 15th cycle and two reduction waves are observed at 360 and -180 mV. After completion of polymerization the coated film was washed with deionized water and then cycled in monomer free electrolyte. There was no change in the film character. The scan rate varied from 50 to 250 mV s⁻¹ (Fig. 5) and the film wave current increased with increase in scan rate (Fig. 3). These

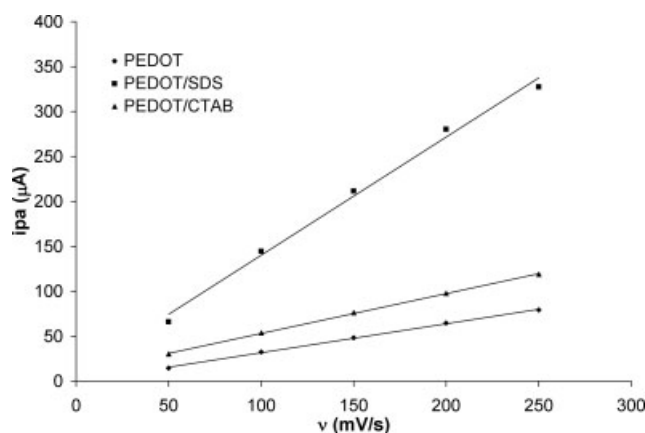


Figure 3 Plot of anodic peak current versus scan rate

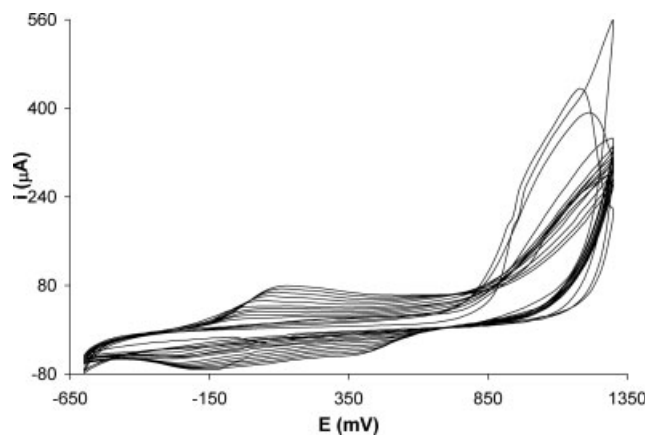


Figure 4 Cyclic voltammogram of 0.01M EDOT with 0.01 SDS in aqueous 0.1M KCl on GCE scan rate 50 mV/s

factors confirmed the formation of good adherent electroactive polymer.

Electropolymerisation of 0.01M EDOT was also performed by cycling the potential between -0.6 and 1.3 V versus SCE at a scan rate of 50 mV s⁻¹ in 0.001M CTAB and 0.1M KCl in deionized water. The irreversible oxidation of EDOT was observed at a 780 mV, which was same as that observed for EDOT in presence of SDS (Fig. 6). The film was washed and cycled in monomer free electrolyte as with SDS. Here also no change in the film character was observed. When the scan rate was varied from 50 to 250 mV s⁻¹ (Fig. 7) there was an increase in the film wave current. In this case also good adherent electroactive polymer was formed. In the subsequent cycles, polymer redox started appearing at lower potentials indicating the formation electroactive

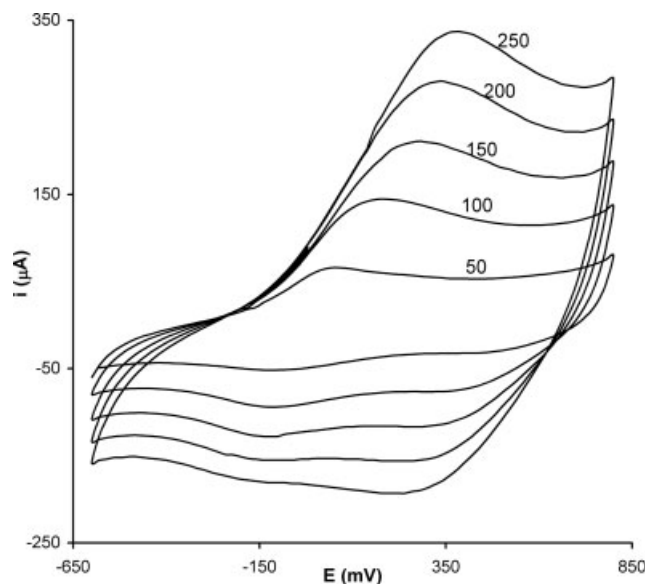


Figure 5 Cyclic voltammogram of EDOT/0.01SDS/KCl film in 0.1M KCl scan rate variation from 50 to 250 mV/s

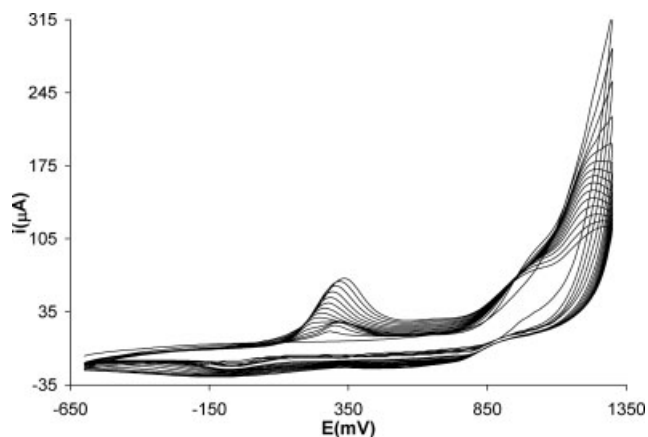


Figure 6 Cyclic voltammogram of 0.01M EDOT with 0.001 CTAB in aqueous 0.1M KCl on GCE scan rate 50 mV/s

polymer growth on the electrode. Interestingly, the polymer oxidation was observed at 340 mV, which is 200 mV higher than that of PEDOT synthesized in presence of SDS. This higher polymer oxidation potential may be the result of formation of a polymer with a less conjugation than that of PEDOT/SDS. PEDOT with bulky groups substituted on the backbone showed the same behavior.³⁰

Spectroelectrochemistry of PEDOT/SDS and PEDOT/CTAB

Spectroelectrochemistry of potentiostatically synthesized PEDOT/SDS and PEDOT/CTAB thin films were carried out in 0.1M KCl in deionized water at

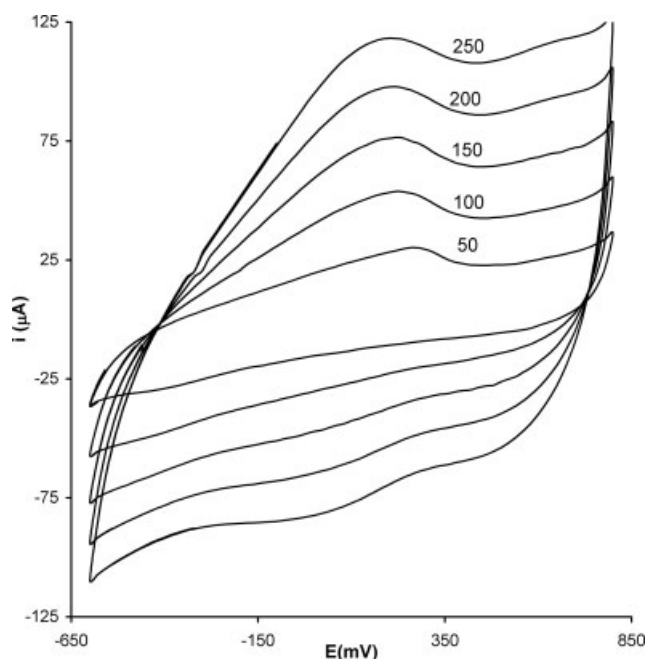


Figure 7 Cyclic voltammogram of EDOT/0.001CTAB/KCl film in 0.1M KCl scan rate variation from 50–250 mV/s

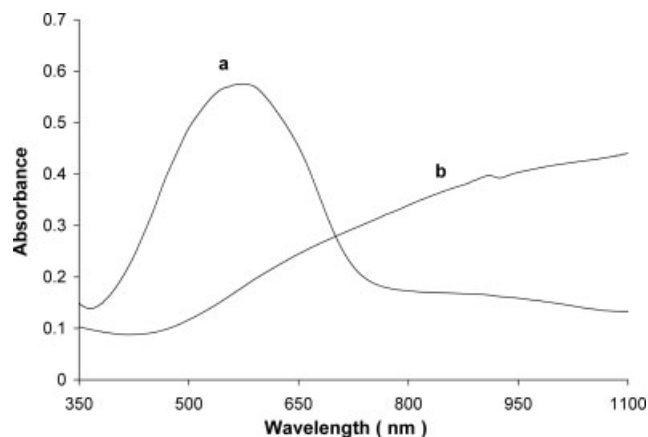


Figure 8 Spectroelectrochemical behavior of PEDOT/SDS in 0.1M KCl at (a) -1.0 V (b) at 1.0 V

various potentials from -1.0 V to 1.0 V present in Figure 8. The PEDOT/SDS polymer was reduced at an applied potential -1.0 V and exhibited a broad band around 561 nm. This absorption is associated to the $\pi-\pi^*$ transition.¹⁰ The polymer was doped by increasing the potential from -1.0 V to $+1.0$ V. During the doping, the absorbance of the peak around 561 nm decreases and a peak at 880 nm grows in intensity. When the applied potential was changed to 1.0 V PEDOT got oxidized completely and showed a broad band at higher wavelength. The *in situ* studies showed that the deposited PEDOT film was opaque blue at -1.0 V and the film was transparent blue at 1.0 V. Figure 9 shows the *in situ* spectra of PEDOT/CTAB at various applied potentials in 0.1M KCl. At

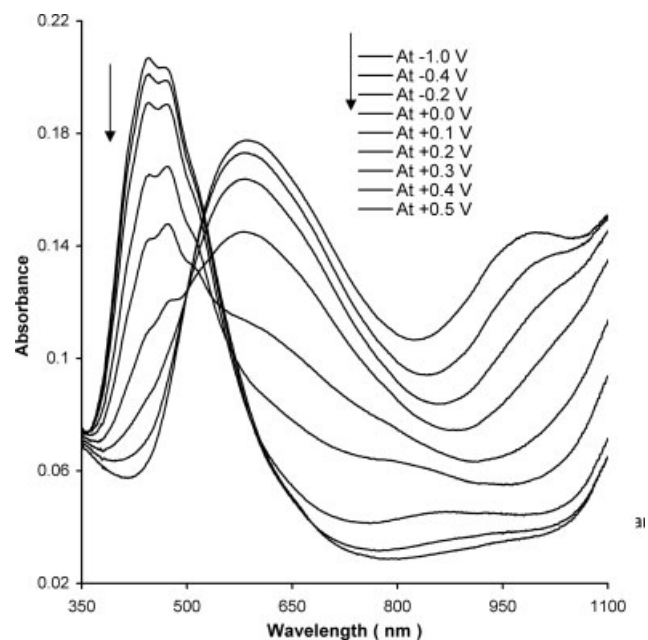


Figure 9 Spectroelectrochemical behavior of PEDOT/CTAB in 0.1M KCl at various applied potentials from -1.0 V to $+0.5$ V

−1.0 V the polymer was transparent yellow in color. The polymer absorbed at 436 and 465 nm, which might be because of the π - π^* transitions. The hypsochromic shift in the π - π^* transition confirmed the decrease in conjugation when the polymer was synthesized in presence of CTAB. The absorbance of this peak decreased upon increase in potential from −1.0 V to +1.0 V. A new band appeared around 573 nm at the applied potential 0.2 V and then the absorbance of this band increased as the potential increased from 0.3 V to 0.5 V. Opaque blue color was observed at +1.0 V. Multichromism has been achieved in PEDOT and its derivatives only by the polymerization of synthetically modified EDOT monomers. Herein, we have achieved multichromic PEDOT by synthesizing the polymer in presence of a cationic surfactant.

Optical contrast is probably the most important factor in evaluating an electrochromic material. It is percent transmittance change ($\Delta\%T$) at a specified wavelength where the electrochromic material has the highest optical contrast. The polymeric film was stepped between its reduced and oxidized states. While the film was switched, the percentage transmittance at λ_{max} (573 nm) was monitored as a function of time. The contrast is given as the difference between the reduced and oxidized states and reported as $\Delta\%T$ and the results are presented in Table I. The results reveal good optical contrast and are comparable with the reported values for Poly(3,4-ethylenedioxythiophene) (64%) and poly(3,4-propylenedioxythiophene) (89%).^{11,31} The coloration efficiency is another important parameter, which measures the power requirements of an electrochromic material. In essence, it determines the amount of optical density change (ΔOD) induced as a function of the injected/ejected electronic charge (Q_d), i.e., the amount of charge necessary to produce the optical change. The controlled potential coulometry was employed to evaluate the coloration efficiency and response time^{32,33} and the results are presented in Table I. The values obtained are comparable with the previous literature values.^{32,33} Employing cyclic voltammetry tested the film stability.

TABLE I
Electrochromic Parameters of Copolymers

Parameters	Poly (EDOT)/SDS	Poly (EDOT)/CTAB
Coloration efficiency ($\text{cm}^2 \text{C}^{-1}$), η	582	645
Response time (s), τ		
Coloring	10	12
Bleaching	14	17
Optical contrast ($\Delta\%T$)	69	78

For all the parameters the wavelength is λ_{573} (nm).

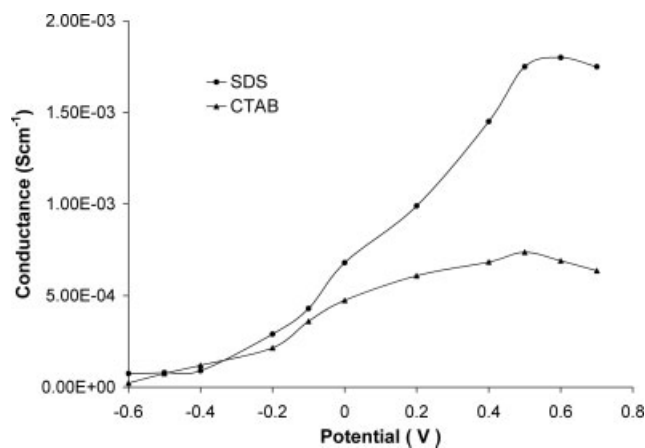


Figure 10 The *in situ* conductance plot of PEDOT/SDS and PEDOT/CTAB polymer film.

The potential cycling between −1000 mV to 1500 mV at scan rate 50 mV s^{-1} was carried out and the changes were observed in the redox responses. The copolymer film exhibited no significant change in the redox behavior during cycling up to 500 cycles. This suggests good stability of the polymer film.

In situ conductance and surface morphology of PEDOT/SDS and PEDOT/CTAB

In situ conductance of the electrochemically synthesized polymer was measured by following the procedure. Electrosynthesis of PEDOT/SDS was carried out on interdigitated microelectrode by cycling the potential from −0.6 V and 1.3 V, from 0.01M EDOT, 0.01M SDS, and 0.1M KCl in water. The polymer bridged the two working electrodes separated by $15 \mu\text{m}$ in 30 cycles. The *in situ* conductance was measured at applied potentials ranging from −0.6 V to 0.7 V. The polymer was resistive at −0.6 V ($7.5 \times 10^{-5} \text{ S cm}^{-1}$), which indicated that the polymer was in reduced state. The conductance started increasing while the potential was increased and reached a maximum conductance of $1.7 \times 10^{-3} \text{ S cm}^{-1}$ at 0.5 V and the conductance remained same till 0.7 V (Fig. 10). Approximately two orders of change in conductance were observed during doping-dedoping cycle.

To measure the *in situ* conductance of PEDOT/CTAB the polymer was synthesized from 0.01M EDOT, 0.001M CTAB, and 0.1M KCl in water on interdigitated microelectrodes. The polymer bridged the two working electrodes which were separated, but low conductivity was observed while comparing this with PEDOT/SDS. This indicated the high resistive polymer formation, which might be because of the formation of polymer with decreased conjugation length. The polymer conductivity range was 2.3×10^{-5} – $6.36 \times 10^{-4} \text{ S cm}^{-1}$ at the applied potential between −6.0 V and 0.7 V (Fig. 10). The polymer

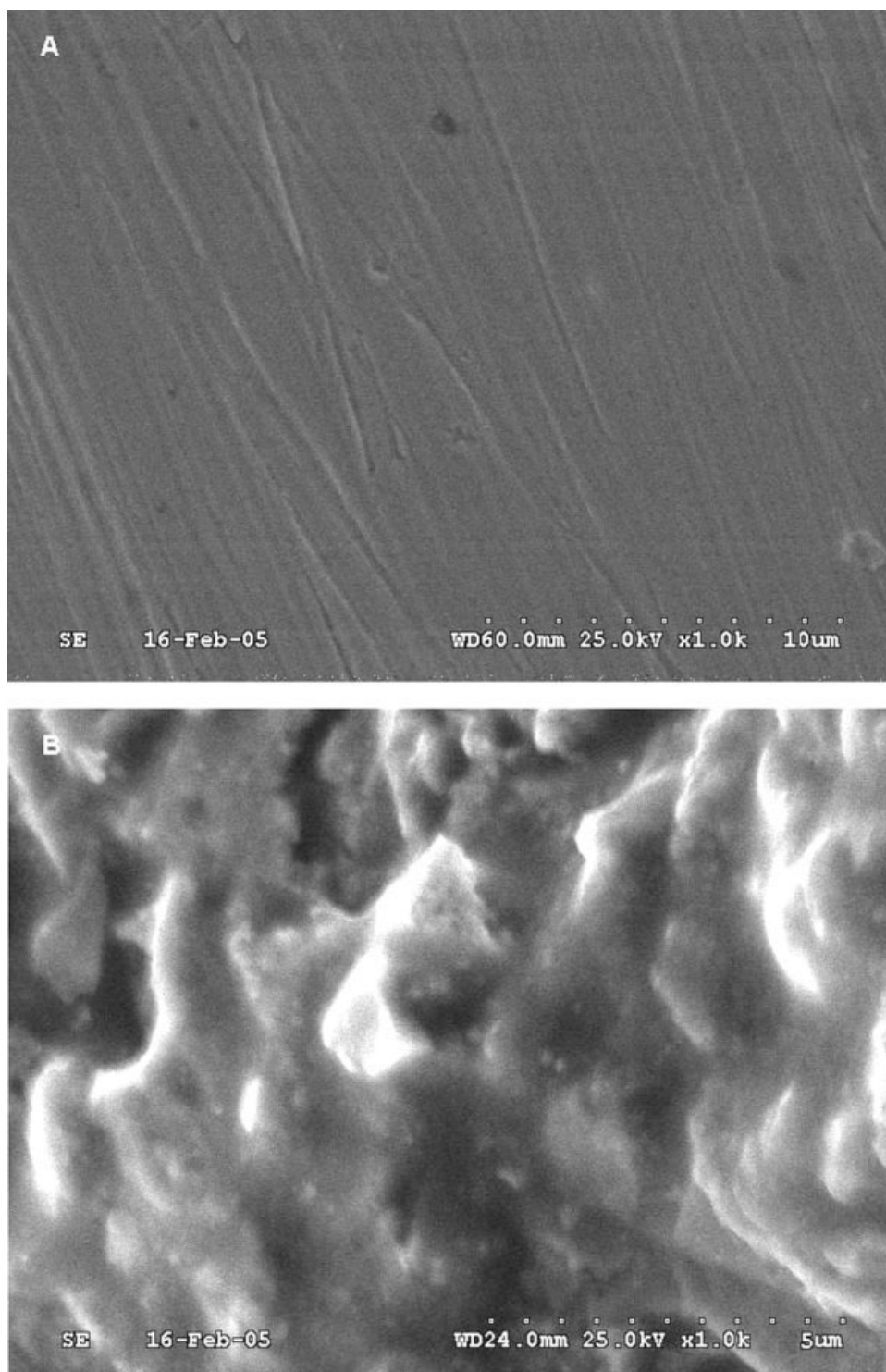


Figure 11 SEM photograph of (A) PEDOT/SDS/KCl surface (B) PEDOT/CTAB/KCl surface

synthesized in presence of anionic surfactant and in absence of any surfactant is opaque blue in the reduced state and transparent blue in the oxidized state. Therefore, we conclude that the decrease in conjugation is because of the interaction between the cationic surfactant and the cation radical formed during the polymer growth.

Figure 11A shows scanning electron micrographs of PEDOT/SDS/KCl obtained on glassy carbon electrode surface prepared by potential cycling method. The SEM photograph exhibits a homogeneous and smooth adherent fiber-like polymer surface. The smooth adherent films indicate the electroactive nature of conducting polymer film. Slight difference is

observed in the form of the PEDOT/SDS with PEDOT + LiClO₄. The LiClO₄ used PEDOT surface exhibited a homogeneous and smooth adherent film as already reported by Vasantha and Phani²⁰ Figure 11(B) result in the formation of a “sponge” like structure of PEDOT/CTAB/KCl with diameters 5 μm. The sponge-like structure contains voids but less conductivity of CTAB doped polymer film this is further conformation of less conjugation.

CONCLUSIONS

A new poly(3,4-ethylenedioxythiophene) counter electrode polymer was synthesized by electroinitiation in the presence of a cationic surfactant, CTAB and characterized by cyclic voltammetry, spectroelectrochemistry, and *in situ* conductance measurement. This polymer exhibited good dual electrochromic behavior and was transparent yellow in the reduced state and opaque blue in the oxidized state. Tedious procedure reported for the designing of counter electrode polymer was made simple by electropolymerising EDOT in the presence of CTAB. The electroactive polymer obtained by the electropolymerization of EDOT using anionic surfactant of SDS also showed electrochromic behavior, opaque blue at -1.0 V and transparent blue at 1.0 V. This polymer showed better conductance than the polymer obtained with CTAB.

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References

- Manisankar, P.; Vedhi, C.; Selvanathan, G.; Somasundaram, R. M. *Chem Mater* 2005, 17, 1722.
- Manisankar, P.; Vedhi, C.; Selvanathan, G. *J Polym Sci Part A: Polym Chem* 2005, 43, 1702.
- Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., Eds. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1998.
- McCullough, R. D. *Adv Mater* 1998, 10, 93.
- Roncali, J. *Chem Rev* 1997, 97, 173.
- Heywang, G.; Jonas, F. *Adv Mater* 1992, 4, 116.
- Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. *Chem Mater* 1998, 10, 896.
- Groenendaal, L.; Zotti, G.; Aubert, P.-H.; Waybright, S. M.; Reynolds, J. R. *Adv Mater* 2003, 15, 855.
- Andersson, P.; Nilsson, D.; Svensson, P.-O.; Chen, M.; Malmstrom, A.; Remonen, T.; Kugler, T.; Berggren, M. *Adv Mater (Weinheim, Germany)* 2002, 14, 1460.
- Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. *Adv Mater* 1999, 11, 1379.
- Krishnamoorthy, K.; Ambade, A. V.; Kanungo, M.; Contractor, A. Q.; Kumar, A. *J Mater Chem* 2001, 11, 2909.
- Gaupp, C. L.; Welsh, D. M.; David Rauh, R.; Reynolds, J. R. *Chem Mater* 2002, 14, 3964.
- Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* 2004, 37, 7559.
- Sakmeche, N.; Aaron, J. J.; Fall, M.; Aeyach, S.; Jouini, M.; Lacroix, J. C.; Lacaze, P.-C. *J Chem Soc Chem Commun* 1996 2723.
- Aeyach, S.; Bazzacui, El. A.; Lacaze, P. C. *J Electroanal Chem* 1997, 434, 153.
- Gningue-Sall, D.; Fall, M.; Dieng, M. M.; Aaron, J. J.; Lacaze, P.-C. *Phys Chem Chem Phys* 1999, 1, 1731.
- Ray, A. K.; Saha, A.; Mukherjee, A. K. *Chem Phys Lett* 2005, 401, 72.
- Jonas, F.; Morrison, J. T. *Synth Met* 1997, 85, 1397.
- Tsakova, V.; Winkels, S.; Schultze, J. W.; *Electrochimica Acta* 2000, 46, 759.
- Vasantha, V. S.; Phani, K. L. N. *J Electroanal Chem* 2002, 520, 79.
- Choi, J. W.; Han, M. G.; Kim, S. Y.; Oh, S. G.; Im, S. S. *Synth Met* 2004, 141, 293.
- Sadki, S.; Chevrot, C. *Electrochimica Acta* 2003, 48, 733.
- Manisankar, P.; Vedhi, C.; Selvanathan, G.; Gurumalles Prabu, H. *Electrochimica Acta* 2006, 51, 2964.
- Schwendeman, I.; Hickman, R.; Sonmez, G.; Schottland, P.; Zong, K.; Welsh, D. M.; Reynolds, J. R. *Chem Mater* 2002, 14, 3118, .
- Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chem Mater* 1998, 10, 2101.
- Rauh, R. D.; Wang, F.; Reynolds, J. R.; Meeker, D. L. *Electrochimica Acta* 2001, 46, 2023.
- Stefan Meskers, C. J.; Jeroen van Duren, K. J.; Rene Janssen, A. J.; Frank, L.; Groenendaal, B. L. *Adv Mater (Weinheim, Germany)* 2003, 15, 613.
- Schwendeman, I.; Hwang, J.; Welsh, D. M.; Tanner, D. B.; Reynolds, J. R. *Adv Mater* 2001, 13, 634.
- Praus, P. *Talanta* 2005, 65, 281.
- Krishnamoorthy, K.; Ambade, A. V.; Mishra, S. P.; Kanungo, M.; Contractor, A. Q.; Kumar, A. *Polymer* 2002, 43, 6465.
- Krishnamoorthy, K.; Kanungo, M.; Contractor, A. Q.; Kumar, A. *Synth Metals* 2001, 124, 471.
- Giroto, E. M.; De Paoli, M.-A. *J Braz Chem Soc* 1999, 10, 394.
- Ribeiro, A. S.; Gazotti, W. A.; Nogueira, V. C.; Machado, D. A.; dos Santos Filho, P. F.; De Paoli, M.-A. *J Chile Chem Soc* 2004, 49, 197, .