SYNTHESIS OF POLY (3,4-ETHYLENEDIOXYTHIOPHENE) IN PRESENCE OF SURFACTANTS

Dual electrochromic poly (3,4-ethylenedioxythiophene) was synthesized from 3,4-ethylenedioxythiophene in presence of a cationic surfactant cetyl trimethyl ammonium bromide (CTAB). Then the polymer was characterized and compared with poly (3,4-ethylenedioxythiophene) polymer prepared in presence of SDS.

5.1. INTRODUCTION

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 [119]. Polythiophene is a relatively stable conducting polymer but the synthesis by electrochemical initiation is very difficult due to the high oxidation potential of thiophene [120]. This problem has been overcome by the introduction of 3,4-ethylenedioxy groups thiophene. This monomer is oxidized at 1.1 V vs Ag/Ag⁺, which is 1 V less than that of thiophene. 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 [121]. These interesting properties attracted the attention of researchers from academic and industrial labs that resulted in application of this polymer in various devices. 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 [122]. Most of the research on PEDOT is focused on to improve the electrochromic properties. Reynolds and co-workers synthesized various derivatives of EDOT and improved the contrast of the polymer to 78% in case of dimethyl substituted poly(3,4-propylenedioxythiophene) [123]. Very recently, Kumar and co-workers synthesized and
characterized a dibenzyl substituted poly (3,4-propylenedioxythiophene) that exhibited the highest contrast (89%) reported till date [124]. Reynolds and co-workers 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. 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 [125-127]. IR electrochromic devices were fabricated by the same group and others [128, 129]. Thus the above researches conclude that a counter electrode polymer, which has a higher band gap, is a must for the better device fabrication. Till date the counter electrode polymers were synthesized using tedious synthetic procedure.

5.2. ELECTROCHEMICAL POLYMERIZATION

Growth of PEDOT (Fig. 5.1) was studied in aqueous 0.1M KCl media in the potential range from -600 to 1300 mV at a scan rate of 50 mVs \(^{-1}\) using cyclic voltammetry. One well-defined oxidation peak around 1240 mV was observed in the first cycle while a new oxidation peak around 400 mV and a reduction peak around 440 mV were observed after three-cycles in the cyclic voltammograms. The intensity of the newer peaks increased with increase in the number of potential cycle indicating a formation and continuous growth of PEDOT on the electrode. A blue color PEDOT was seen on the electrode after the completion of 15 cycles, The formed polymer was washed with deionised water and cycled between -600 and 800 mV in the monomer free electrolyte. As the scan rate increased the peak current increased linearly suggesting adherent film (Fig.5.2). anionic surfactant, SDS is a commonly used surfactant in polymerization [130]
0.01 M EDOT monomer was electropolymerised in presence of anionic surfactant of 0.01 M SDS and 0.1 M KCl in aqueous medium by cycling the potential at 50 mVs⁻¹ between -600 and 1300 mV versus SCE. The monomer oxidation peak starts at 720 mV and peaks at 1120 mV (Fig. 5.3). 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 a monomer free electrolyte. There was no change in the film character. The scan rate was varied from 50-250 mVs⁻¹ (Fig. 5.4) and the film wave current increased with increase in scan rate. These factors confirmed the formation of good adherent electroactive polymer.

Electropolymerisation of 0.01 M EDOT was also performed by cycling the potential between -600 and 1300 mV vs. SCE at a scan rate of 50 mVs⁻¹ in 0.001 M CTAB and 0.1M KCl in deionized water. The irreversible oxidation of EDOT was observed at 780 mV, which was same as that observed for EDOT in presence of SDS (Fig. 5.5). 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 50-250 mVs⁻¹ (Fig. 5.6) 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 peaks started appearing at lower potentials indicating the formation electroactive 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 similar behaviour [131].
5.2.1. Spectroelectrochemistry of PEDOT/SDS and PEDOT/CTAB

Spectroelectrochemical studies of potentiostatically synthesized PEDOT/SDS and PEDOT/CTAB thin films were carried out in 0.1 M KCl in deionized water at various potentials from -1000 mV to 1000 mV and the spectroelectrochemical behaviour is presented in figure 5.7. The PEDOT/SDS polymer was reduced at an applied potential -1000 mV and exhibited a broad band around 561 nm. This absorption is associated to the π - π* transition. The polymer was doped by increasing the potential from -1000 mV to 1000 mV. During the doping, the absorbance of the peak around 561 nm decreased and a peak at 880 nm grew in intensity. When the applied potential was changed to 1000 mV, PEDOT got oxidized completely and showed a broad band at higher wavelength. The insitu studies showed that the deposited PEDOT film was opaque blue at -1000 mV and the film was transparent blue at 1000 mV. Figure 5.8 shows the in situ spectra of PEDOT/CTAB at various applied potentials in 0.1 M KCl. At -1000 mV the polymer was transparent yellow in color. The polymer absorbed at 436 and 465 nm, which might be due to 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 -1000 mV to 1000 mV. A new band appeared around 573 nm at the applied potential 200 mV and then the absorbance of this band increased as the potential increased from 300 mV to 500 mV. Opaque blue color was observed at 1000 mV. 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.

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 5.1. 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%) [132]. The controlled potential coulometry was employed to evaluate the coloration efficiency and response time [133, 134] and the results are presented in table 5.1. The values obtained are comparable with the previous literature values [133, 134]. Employing cyclic voltammetry tested the film stability. The potential cycling between $-1500$ mV to $1500$ mV at scan rate $50$ mVs$^{-1}$ 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 500 cycles. This suggests good stability of the polymer film.

Table 5.1. Electrochromic parameters of copolymers

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Wavelength (nm)</th>
<th>PEDOT/SDS</th>
<th>PEDOT/CTAB</th>
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<tbody>
<tr>
<td>Coloration efficiency</td>
<td>$\lambda_{573}$</td>
<td>582</td>
<td>645</td>
</tr>
<tr>
<td>Response time (s), $\tau$</td>
<td>$\lambda_{573}$</td>
<td>Coloring</td>
<td>10</td>
</tr>
<tr>
<td>Optical contrast ($\Delta%T$)</td>
<td>$\lambda_{573}$</td>
<td>Bleaching</td>
<td>14</td>
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5.2.2. In situ Conductance 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 $-600$ V and $1300$ mV from $0.01$ M EDOT, $0.01$ M SDS and $0.1$ M KCl in water. The polymer bridged the two working electrodes separated by $15\mu$ in 30 cycles. The in situ conductance was measured at applied potentials ranging from $-600$ V to $700$ mV. The polymer was resistive at

82
−600 mV (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 500 mV and the conductance remained same till 700 mV (Fig. 5.9). Approximately two orders of change in conductance were observed during doping-dedoping cycle.

In order to measure the in situ conductance of PEDOT/CTAB the polymer was synthesized from 0.01 M EDOT, 0.001 M CTAB and 0.1 M KCl in water on interdigitated microelectrodes. The polymer bridged the two working electrodes separated but low conductivity was observed while comparing this with PEDOT/SDS. This indicated the high resistive polymer formation, which might be due to the formation of polymer with decreased conjugation length. The polymer conductivity range was 2.3 \times 10^{-5} \text{ to } 6.36 \times 10^{-4} \text{ S cm}^{-1} at the applied potential between −600 and 700 mV (Fig. 5.9). The polymer synthesized in presence of anionic surfactant and in the 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 due to the interaction between the cationic surfactant and the cation radical formed during the polymer growth.

5.2.3. Surface Morphology of PEDOT/SDS and PEDOT/CTAB

Figure 5.10A 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 Phani coworkers [135]. Figure 5.10B results 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 may be due to lesser conjugation.

5.3. 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 behaviour 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.
Fig. 5.1. Cyclic voltammogram of 0.01 M EDOT in aqueous 0.1 M KCl on GCE scan rate 50 mVs$^{-1}$

Fig. 5.2. Cyclic voltammogram of PEDOT/KCl film in 0.1 M KCl scan rate variation from 50 - 250 mVs$^{-1}$

Fig. 5.3. Cyclic voltammogram of 0.01 M EDOT with 0.01 SDS in aqueous 0.1 M KCl on GCE scan rate 50 mVs$^{-1}$
Fig. 5.4. Cyclic voltammogram of EDOT/0.01SDS/KCl film in 0.1M KCl scan rate variation from 50 - 250 mVs⁻¹

Fig. 5.5. Cyclic voltammogram of 0.01 M EDOT with 0.001 CTAB in aqueous 0.1M KCl on GCE scan rate 50 mVs⁻¹

Fig. 5.6. Cyclic voltammogram of EDOT/0.001CTAB /KCl film in 0.1M KCl scan rate variation from 50 - 250 mVs⁻¹
Fig. 5. 7. Spectroelectrochemical behaviour of PEDOT/SDS in 0.1 M KCl at (a) -1000 mV (b) at 1000 mV

Fig. 5.8. Spectroelectrochemical behaviour of PEDOT/CTAB in 0.1 M KCl at various applied potentials from -1000 mV to 500 mV.

Fig. 5.9. The in situ conductance plot of PEDOT/SDS and PEDOT/CTAB polymer film
Fig. 5.10. SEM photographs of (A) PEDOT/SDS/KCl surface (B) PEDOT/CTAB/KCl surface