Electrochemical Synthesis, Characterization and Electrochemical behaviour of New Conducting Copolymers of 2-methoxyaniline-co-2,3-dihydrothieno[3,4-b][1,4]dioxine-2-carboxylic acid

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Abstract

Electroactive conducting copolymers of 2-methoxyaniline and 2,3-dihydrothieno[3,4-b][1,4]dioxine-2-carboxylic acid (EDOT carboxylic acid) molecules were prepared in non-aqueous solution by electrode potential cycling. Copolymerization was carried out at different feed concentrations of the monomers on a gold electrode. Four different feed concentrations were used to prepare four different copolymers. The obtained copolymers were characterized with cyclic voltammetry and infrared spectroscopy. The prepared hompolymers and copolymers were investigated with in situ conductivity measurements. Two transitions were observed in the in situ conductivities of the copolymers.

Keywords: in situ conductivity, 2-methoxyaniline, EDOT carboxylic, copolymers

1. Introduction

Recently, electrically conducting polymers have many potential applications, such as new materials for battery electrodes (Otero & Cantero 1999, Amanokura et al. 2001, Gurunathan et al. 1999), supercapacitors (Mastragostino et al. 2002), chemical sensors (Gupta et al. 2006, Sotzing et al. 2000, Lin et al. 1999, Nicolas-Debarnot et al. 2003). ion sieving (Shinohara et al. 1986), corrosion protection (Ohtsuka 2012, Garca et al. 2002), and microwave shielding (Patil et al. 2012, Buckley & Eashov 1996). Among conducting polymers, poly(2-methoxyaniline) (PMA) has attracted much attention. Bereket et al. (2005) have been studied its anti-corrosive properties. Chaudhari and Patil (2008) have been investigated the corrosion protective of bi-layered composites of polyaniline and PMA on low carbon steel. PMA have been synthesized for developed for development of glucose biosensor (Savale & Shirsat 2009). The corrosion-protective performance of nano POA/alkyd coatings has been investigated on mild steel (Jadhav et al. 2010).

Copolymerization of two different monomers that bear different functional groups leads to modified copolymers that possessing interesting properties. several studies included copolymerization of aniline-thiophene, furan-thiophene and aniline-pyrrole monomers have been reported recently (Arjomandi & Holze 2008, Alakhras & Holze 2008, Vogel & Holze 2005, Antony & Jayakannan 2011). The primary advantage of copolymerization is that it leads to a material in which its properties can be regulated by adjusting the ratio of the concentration of monomers in the feed. Thus copolymerization is an important method to modify the properties of individual homopolymers.

In the present study, 2-methoxyaniline (MA) and EDOT carboxylic acid (EDOTCA) have been se-lected as monomers for performing electrochemical copolymerization (Figure 1) in 0.1M Tetrabutylammonium tetrafluoroborate (TBATFB)/acetonitrile medium. Cyclic voltammetry was used to deposit polymeric films on gold working electrode and sub-sequent characterization. Copolymers were also characterized by Infrared spectroscopy. The copolymers and homopolymers were investigated by in situ conductivity measurements.

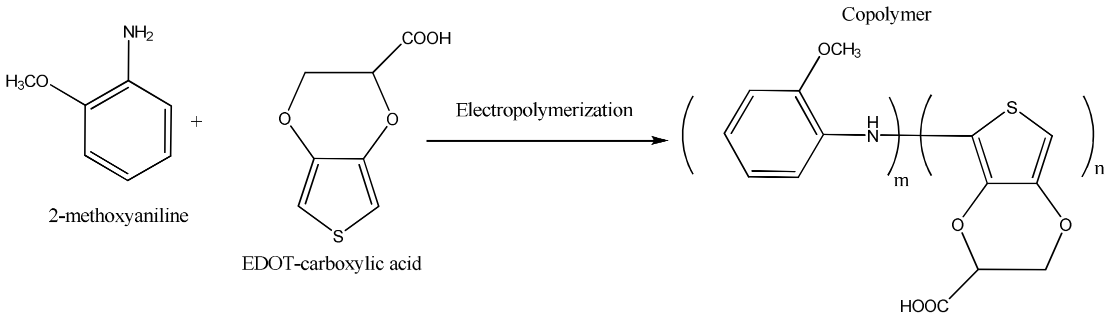

Figure 1. Electrochemical coolymerization of MA and EDOTCA molecules.

2. Experimental

All chemicals were of analytical grade. The 2-methoxyaniline (Fluka) and EDOT-carboxylic acid (Aldrich) used as received. Tetrabutylammonium tetrafluoroborate (TBATFB; Aldrich, Stein-heim, Germany; 99%) was dried in vacuo at 80ºC for 24 h. Acetonitrile (Merck, Darmstadt, Germany; anhydrous, <10 ppm H2O) was used without further purification.

The electropolymerization was performed under potentiodynamic conditions at a scan rate of 100 mV/s and by using 0.1M TBATFB in acetonitrile as supported electrolyte and in a one-compartment, three-electrode cell at room temperature. The working electrode used is gold disc electrode, the counter electrode is platinum wire and the reference electrode is Ag/AgCl (which has a potential of +0.22 vs SHE). The working gold disk electrode (0.2 cm2) was polished down to 0.3 µ with Al2O3, rinsed with; acetone, distilled water and finally with ethanol. Cyclic voltammetry was performed with a computerized SP50 potentiostat (from Bio Logic Science Instruments, France). All solutions were freshly prepared, purged with nitrogen (99.999%), and all experiments were performed at room temperature (20 ˚C).

The Fourier transform infrared (FTIR) spectra of the homopolymer and copolymer films were recorded with KBr pellets with a PerkinElmer FTIR 1000 spectrometer at a 2 cm-1 resolution. For these measurements, the film was scraped off from the electrode and dried.

In the In situ conductivity measurements the polymer was deposited on a two-strips gold electrode in a three electrode cell with a specially designed electronic circuit supplying 10 mV DC voltage across the two gold strips (Holze and & Lippe 1990). In this measurements the two gold strips of the electrode are separated by a gap of a few micrometers that is easily bridged through deposition of conducting polymers, when both electrodes are connected electrically together and used as the working electrode. Although this setup is associated with the problem of ensuring the identical thicknesses of films across the insulating gap, nevertheless, approximately reproducible results can be obtained by adjusting the experimental conditions as very thin films can usually form good bridges over the gap between the electrodes.

3. Results and Discussion

3.1 Electrochemical oxidation of OA and EDOTCA

Figure 2 shows the electrooxidation of MA (10 mM) in 0.1 M TBATFB solution when cycling the potential between -0.2 and 1.50 V at a scan rate of 100 mV/s. In the positive sweep one anodic peaks are well defined at 0.934 V is caused by the oxidation of –NH2 of MA. The anodic peak due to electro oxidation of 10 mM MA started around +0.673 V (versus Ag/AgCl), in 0.1 M TBATFB/acetonitrile solution. The oxidation peak of MA at platinum working electrode were reported by Ozyilmaz et al. (2008) at +0.93 V for low scan rate and at approx. +1.21V for high scan rate which is in perfect agreement with our result. On the negative sweep the cyclic voltammogram is not showing any corresponding reduction peaks.

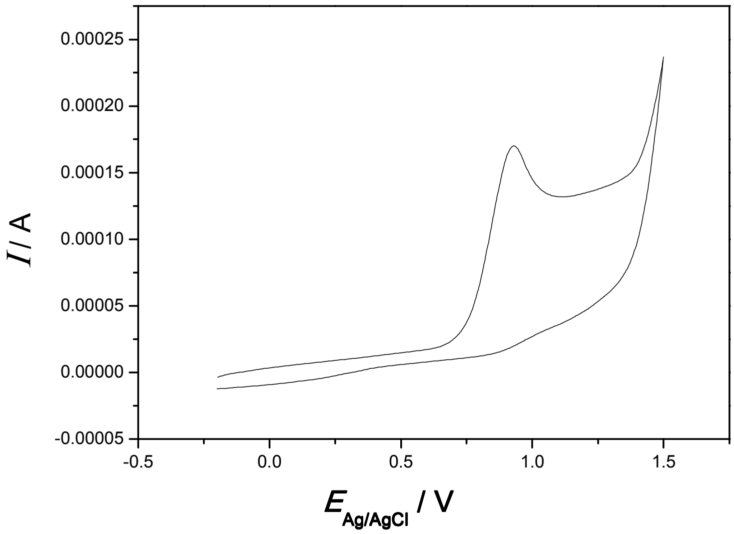

Figure 2. Cyclic voltammogram for electrolysis of solution containing 10 mM MA in 0.1 M TBATFB in acetonitrile by cycling the potential between -0.2 and 1.5 V at a scan rate of 100 mV/s.

Figure 3 shows the electro-oxidation of EDOTCA (10 mM) in 0.1 M TBATFB/ acetonitrile solution when cycling the potential between -0.3 and 1.6 V at a scan rate of 100 mV/s. In the positive sweep one anodic peaks are well defined at 1.549 V is caused by the oxidation of the sulfur atom of EDOTCA. The position of this anodic peak is higher with 19 mV than that reported by Ocampo et al. (2006) for the oxidation of 10 mM 3,4-ethylenedioxythiophene (EDOT) in a solution of 0.1 M LiClO4 in acetonitrile and at steel electrode. Ocampo et al. (2006) also reported that a second anodic peak corresponds to the oxidation of EDOT located at higher potential value and overlaps with the oxidation of the medium. Both, the anodic peak that observed in this study for EDOTCA and the one that obtained by Ocampo et al.(2006) for EDOT are higher than that reported elsewhere (Saraç et al. 2003, Vasantha & Phani 2002). All of the differences between the position of the anodic potential that observed in our study for EDOTCA and that reported for EDOT in previous works can be attributed to two reasons. The first one is the structural difference between EDOT and EDOTCA. The second one is that we used in our experiments a different supporting electrolyte and working electrode than that used in the reported works for electrochemical behavior of EDOT.

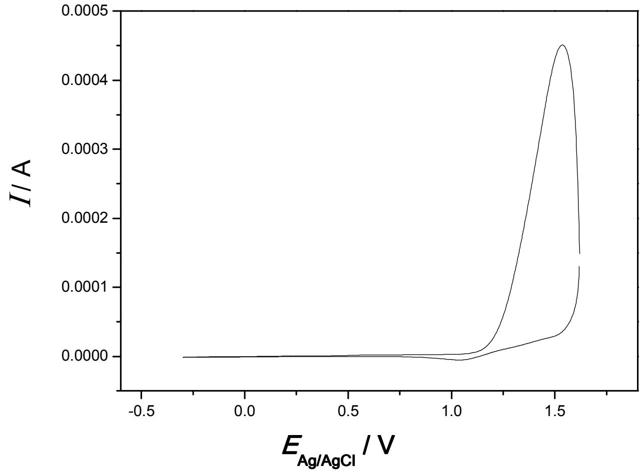

Figure 3. Cyclic voltammogram for electrolysis of solution containing 10 mM EDOTCA in 0.1 M TBATFB in acetonitrile by cycling the potential between -0.3 and 1.6 V at a scan rate of 100 mV/s.

3.2 Electrochemical homopolymerization of MA

The multisweep cyclic voltammograms (40 cycles) of 1 mM MA in 0.1 M TBATFB/acetonitrile solution at gold electrode are displayed in Figure 4. It was observed from Figure 4 that the oxidation peak of the MA in the first cycle disappears and anew anodic and cathodic currents increase in the potential region between -200.0 and 1.07

V with each subsequent cycle. Obviously, These currents are corresponding growth of the PMA films at the gold surface. In the positive sweep in the cycles of Figure 4 an anodic beaks observed at 0.384 and 0.875 V. In the negative sweep the cyclic voltammograms are showing a two corresponding reduction peaks at -0.008 and 0.571 V. These peaks are caused by oxidations and reductions of the polymers films that growth at the gold surface.

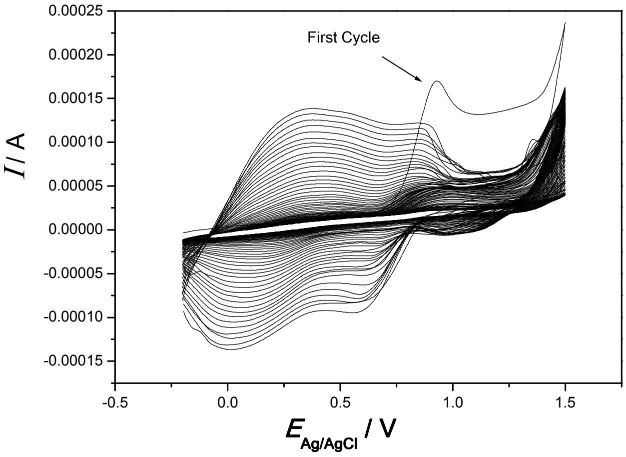

Figure 4. Cyclic voltammograms for electrolysis of solution containing 10 mM MA in 0.1 M TBATFB in acetonitrile by cycling the potential between -0.2 and 1.5 V at a scan rate of 100 mV/s.

The PMA modified electrode was then immersed into monomer free electrolyte solution and its cyclic voltammogram was recorded in the potential range between -0.2 and 1.20 V as depicted in Figure 5. The film was very stable; it did not lose its electrochemical activity after repetitive cycling both at very low and very high scan rates in this potential region. The cyclic voltammogram of the PMA film (Figure 5) shows a two anodic peaks at 0.371 and 1.067 V and its corresponding cathodic waves at 0.217 and 0.707 V. This electrochemical behavior are totally different from the electrochemical behavior of the MA monomers which are described in the Figure 2. This difference is an evidence of the formation of the polymer film at the gold surface. Bereket et al. (2005) reported that the PMA film exhibits one broad oxidation and one reduction peaks in the blank solution. In them results the broad anodic peak was observed in the potential range between 0.3 to 1.6 V which in the potential range of the two anodic peaks that observed in our study. The difference between our result and that of Bereket et al (2003) might be related to the difference in the electrolyte solutions that they used in them experiments from that one we used in this study. In our study we used 0.1 M TBATFB in acetonitrile as supporting electrolyte. The supporting electrolyte used in the experiments of Bereket et al. is 20mM HClO4 in 0.1M tetrabutylammonium perchlorate. The use of this supporting electrolyte might cause an overlap between tow anodic peaks to appear as broad one as reported in the Bereket et al. (2005) result. A two well-resolved anodic peaks in the cyclic voltammograms recorded during the synthesis of PMA film in aqueous solution of H2SO4 as supporting electrolyte are reported elsewhere (Borole et al. 2005). Patil et al. (1997) were reported the difference between the electrochemical behavior of PMA in the presence and absence of NaCl. They obtained a well distinct peaks in the cyclic voltammogram of the PMA that deposited in the presence of NaCl in the deposition medium. While in the absence of NaCl in the the deposition medium they observed that the peaks of the cyclic voltammogram are not well-resolved.

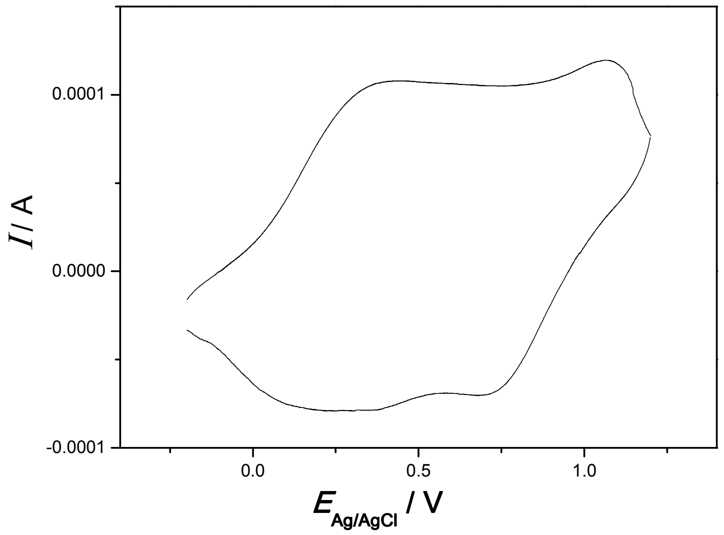

Figure 5. Cyclic voltammograms for electrolysis of PMA in 0.1 M TBATFB/ acetonitrile solution (in monomer free electrolyte solution) at a scan rate of 100 mV/s

3.3 Electrochemical homopolymerization of EDOTCA

Figure 6 shows the multisweep cyclic voltammograms (40 cycles) of 10 mM EDOTCA in 0.1 M TBATFB/acetonitrile solution at gold electrode. The formation and growth of the poly(EDOTCA) polymer (PEDOTCA) film can easily be seen in this figure. The oxidation and reduction peaks of the film increase in intensity as the film grows. In the multisweep cyclic voltammograms of Figure 6 the anodic current that corresponds of the polymer film growth appears in the range between -0.052 and 0.835 V and its corresponding cathodic one appears in the range between -0.285 and 0.686 V. This wide range potential of electropolymerization is also observed in the in the cyclic voltammograms that recorded for electropolymerization of EDOT in different supporting electrolytes and at different working electrodes as reported by several previous works (Ocampo et al. 2006, Saraç et al. 2003, Ahmed et al. 2012).

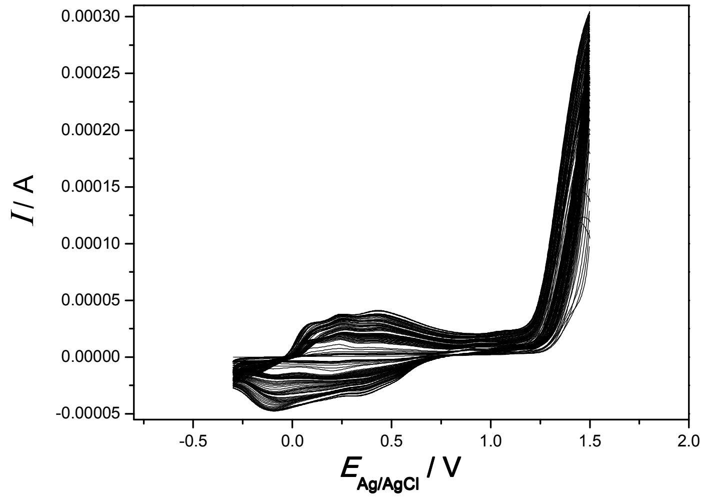

Figure 6. Cyclic voltammograms for electrolysis of solution containing 10 mM EDOTCA in 0.1 M TBATFB in acetonitrile by cycling the potential between -0.3 and 1.5 V at a scan rate of 100 mV/s.

A cyclic voltammogram was recorded for the gold electrode that covered with a layers of the polymer PEDOTCA layers in a monomer free electrolyte solution in the potential range between -0.3 and 1.1 V as shown in Figure 7. The film was very stable; it did not lose its electrochemical activity after repetitive cycling both at very low and very high scan rates in this potential region. The cyclic voltammogram of the PEDOTCA film (Figure 7) shows two anodic peaks at 0.062 V and at 0.541 V and its corresponding cathodic peak at 0.026 V and at 0.423 V. This electrochemical behavior are totally different from the electrochemical behavior of the EDOTCA monomers which are described in the Figure 3. This difference is an evidence of the formation of the polymer film at the gold surface. The two redox processes of Figure 7 located at higher electrode potentials than that reported by Saraç et al. (2003) for poly(EDOT). They polymerized EDOT from a solution of 0.01 M of monomer concentration and in a supporting electrolyte that consist of 0.1 M LiClO4/propylene carbonate at the carbon fibre microelectrode. These condition of polymerization are different from that used in our study for elctropolymerization of EDOTCA. Therefore the two redox processes that observed in our study are located at higher electrode potential than that reported by Saraç et al. Also the presence of carboxylic acid group as substituent in PEDOTCA might be a second reason for the shifts of the two redox processes to a higher electrode potentials as compared to that of poly(EDOT). It should be mentioned that the shape of cyclic voltammogram of the PEDOTCA that obtained in our study is very similar to that reported for poly(EDOT) (Saraç et al. 2003).

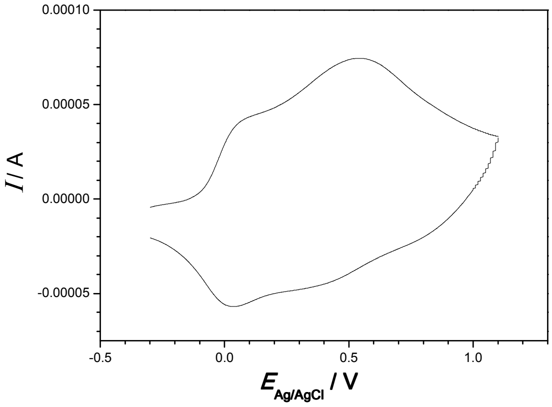

Figure 7. Cyclic voltammograms for electrolysis of PEDOTCA in 0.1 M TBATFB/ acetonitrile solution (in monomer free electrolyte solution) at a scan rate of 100 mV/s

3.4 Electrochemical copolymerization of EDOTCA and MA

We used several different polymerization solutions with different feed ratios to prepare four new copolymers consists of MA and EDOTCA by using cyclic voltammetry method. The copolymers, synthesized with various feed ratios, were labeled copolymer A (COPA, 20mM MA + 5mM EDOTCA), copolymer B (COPB, 20mM MA + 10mM EDOTCA), copolymer C (COPC, 20mM MA + 15mM EDOTCA) and copolymer D (COPD, 5mM MA + 20mM EDOTCA). Figure 8 a-d show the cyclic voltammograms recorded during the synthesis of the above mentioned copolymers. The overall observations and results based on cyclic voltammograms of Figure 8 are concluded as follows. In each case it was observed an anodic and cathodic currents increase with each subsequent cycle. These currents corresponding growth of the copolymers at the gold surfaces. The cyclic voltammograms of Figure 8 are different from that of individual homopolymers (Figure 4 and 6). This difference is notable when the concentration of EDOTCA monomer in the polymerization solution becomes very close to that of MA monomer as in the case of COPB (Figure 8b) and COPC (Figure 8c). When the concen-tration of EDOTCA monomer in the polymerization solution is very low as compared to that of MA monomer the cyclic voltammograms (Figure 8a) becomes very similar to that of homopolymer MA (Figure 4). This indicates that high MA units are incorporated into this copolymer chains. When the concentration of EDOTCA monomer in the polymerization solution is very high as compared to that of MA monomer the cyclic voltammogram (Figure 8d) becomes very similar to that of homopolymerization of EDOTCA (Figure 6). Thus COPD are expected to have more EDOTCA units at the copolymer backbone than that of MA units. Generally in all cases these difference is further supports the formation of copolymers and thus, we got four different copolymers by changing the monomers feed ratios in the polymerization solution.

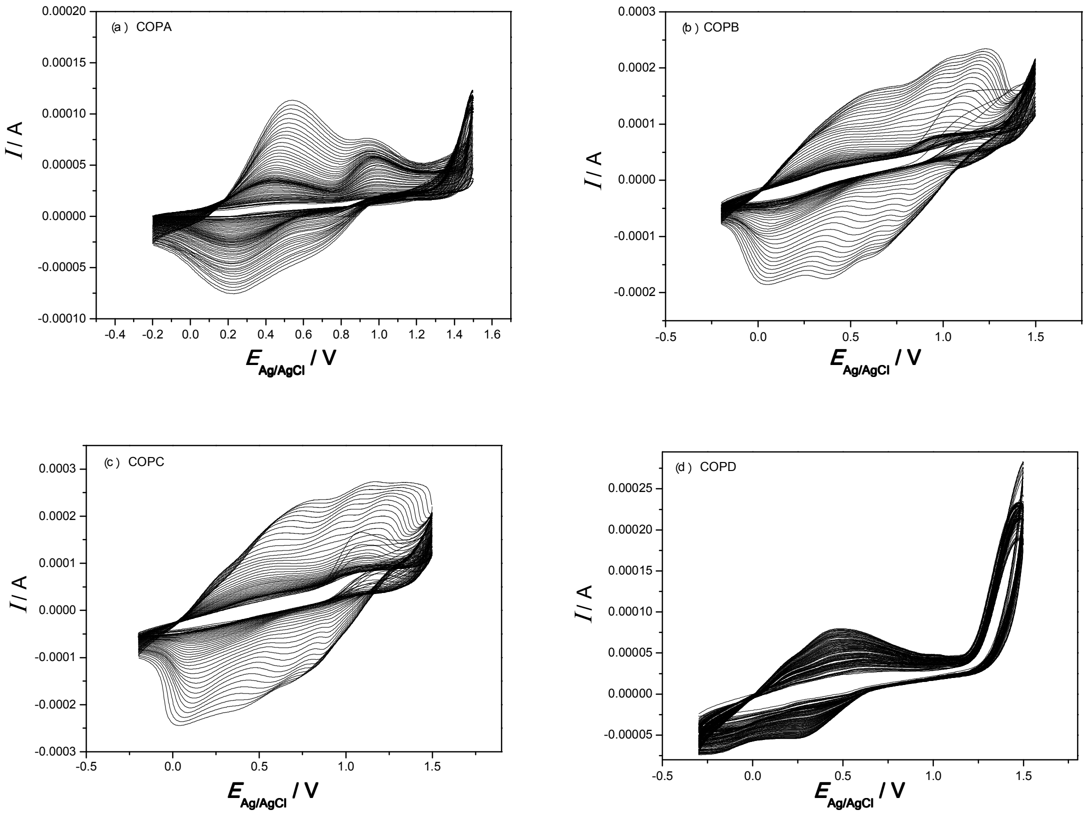

Figure 8. Cyclic voltammograms for electrolysis of solution containing (a) 20 mM MA + 5mM EDOTCA in 0.1 M TBATFB/acetonitrile (b) 20 mM MA + 10 mM EDOTCA in 0.1 M TBATFB/acetonitrile (c) 20 mM MA + 15 mM EDOTCA in 0.1 M TBATFB/acetonitrile (d) 5 mM MA + 20 mM EDOTCA in 0.1 M TBATFB/acetonitrile at a scan rate of 100 mV/s.

To determine the electrochemical behavior of the copolymers COPA, COPB, COPC and COPD a cyclic voltammograms were recorded for the gold electrodes that covered with the layers of each copolymer in a monomer free electrolyte solution. The cyclic voltammograms are shown in Figure 9a-d. Figure 9 shows that the electrochemical behaviors of copolymers COPA, COPB, COPC and COPD are not identical.

Figure 9a shows a typical cyclic voltammogram of a copolymer obtained from a 0.1 M TBATFB/acetonitrile solution containing 20 mM MA and 5 mM EDOTCA. Two overlaps anodic/cathodic peaks couple appear with the copolymer film at a position quite different from the positions observed with PMA (Figure 5) and PEDOTCA (Figure 7). The anodic peaks appear at 0.637 and 0.959 V and its corresponding cathodic peaks appear at 0.276 and 0.535 V. The cathodic and anodic currents of this copolymer are very similar to that found with the homopolymer PMA and higher than that found with the PEDOTCA. This implies that the electrochemical activity (redox capacity) of this copolymer is very close to that of the PMA. The difference between the two anodic/cathodic peak couples positions between COPA and PMA should be attributed to the effects of the presence of small amount of the EDOTCA monomer in the polymerization solution that used in the case COPA. As the concentration of the EDOTCA monomers increased in the feed ratio of the polymerization solution that used for the copolymers, the difference in electrochemical behavior of the copolymers from that of homopolymers becomes notable. This situation is observed in the case of COPB and COPC. A higher current densities corresponding to the anodic and cathodic peaks are observed for the copolymers COPB (Figure 9b) and COPC (Figure 9c) than that of homopolymers (Figure 5 and 7) and other copolymers (Figure 9a and 9d). This implies that the electrochemical activity (redox capacity) is higher for these copolymers. A second observation is that the cyclic voltammograms of these copolymers shows three poorly resolved anodic/cathodic peak couples. The anodic peaks corresponding to the oxidation of COPB appear at 0.539, 0.924 and 1.374 V and its corresponding cathodic peaks appear at 0.045, 0.784 and 1.27 V. For the COPC the anodic peaks appears at 0.484, 1.131 and 1.359 V and its corresponding cathodic peaks appears at -0.096, 0.317 and 1.142 V. When we used higher concentration of the EDOTCA monomers in the feed ratio of the polymerization solution than that of MA monomers as in the case of COPD (Figure 9d), the cyclic voltammogram shows only one anod-ic/cathodic peak couple. The anodic peak appears at 0.604 V and its corresponding cathodic one appears at 0.208 V. The cathodic and anodic currents of this copolymer are very similar to that found with the homopolymer PEDOTCA and lower than that found with the other copolymers.

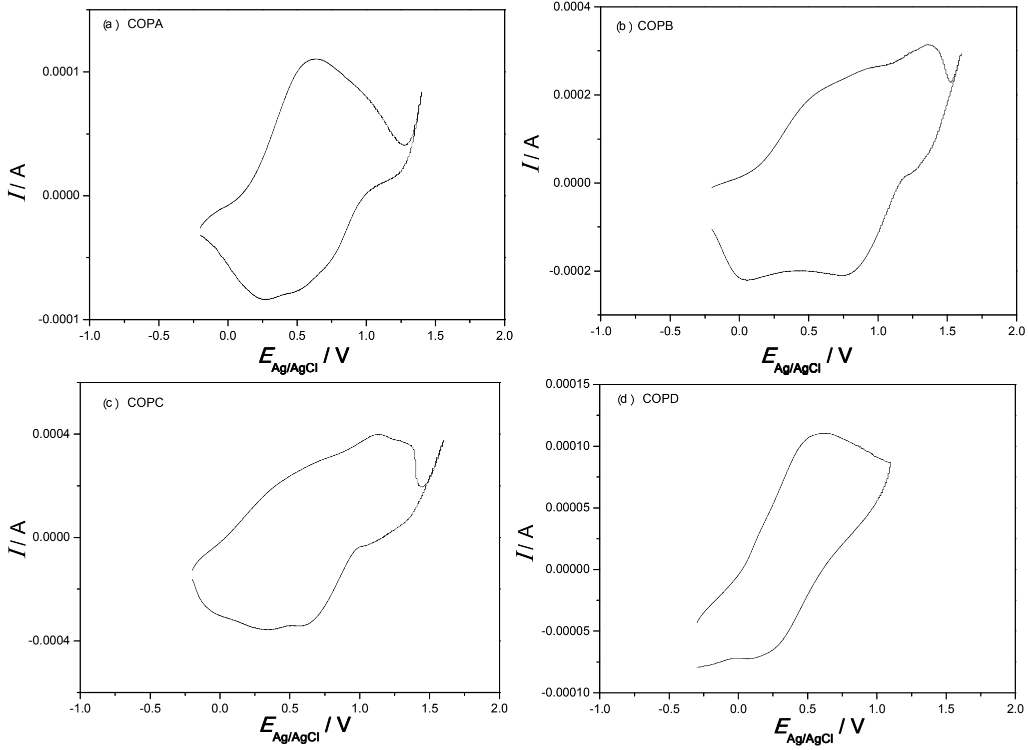

Figure 9. Cyclic voltammograms for the gold electrodes covered with (a) COPA, (b) COPB, (c) COPC and (d) COPD in 0.1 M TBATFB/acetonitrile solution (in monomer free electrolyte solution) at a scan rate of 100 mV/s

3.5 FTIR measurements

The copolymer was characterized by FTIR. The FTIR spectra of PMA, PEDOTCA, COPA, COPB, COPC and COPD are shown in Figure 10a-f. Assignments of the observed bands are listed in Table 1 and based on literature data (Varsányi 1974, Dollish et al. 1974, Lin-Vien et al. 1991, Larkin 2011, Stuart 2004). The spectrum of POA (Figure 9a, Table 1) shows a peaks at 736, 1032, 1045, 1150, 1378 and 1460 cm-1 which are assigned for γ(CH) of aromatic ring, δ(ring), ν(Ph-O-C), ν(C-N-C), δ(CH) of aromatic ring and ν(ring), respectively. In the spectrum of PEDOTCA (Figure 10b, Table 1), there are several peaks appears at 820, 865, 1253, 1503 and 1619 cm-1 that assigned for βas(CH2), thiophene ring breathing, ν(C-O-C) of ethylenedioxy moiety, ν(ring) and ν(ring), respectively. These Peaks are clearly distinguishable from that of POA. Most of the above mentioned characteristic peaks of PMA and PEDOTCA are also appeared in the spectra of the copolymers COPA (Figure 10c), COPB (Figure 10d), COPC (Figure 10e) and COPD (Figure 10f). This feature indicated that these copolymers contains both OA and EDOTCA units. Its was notable that most of the paeks of COPD (Figure 9f) were common for PEDOTCA. This result confirms that the the EDOTCA units are dominant in the copolymer COPD. This conclussion confirms our result that discussed above in the case of electrochemical behaviour of this copolymer. It should be mensitioned that there are two new peaks appeared only in the copolymers spectra. The first one appeared at 693, 688, 694, and 678 cm-1 in the spectrum of COPA, COPB, COPC and COPD, respectively. The second peak appeared at 1585, 1587 and 1584 cm-1 in the spectrum of COPA, COPB and COPC, respectively. Since these peaks are missed in the spectra of the homopolymers it was probably that these peaks are concerning the intramolecular interaction between MA and EDOTAC units at the copolymers backbone.

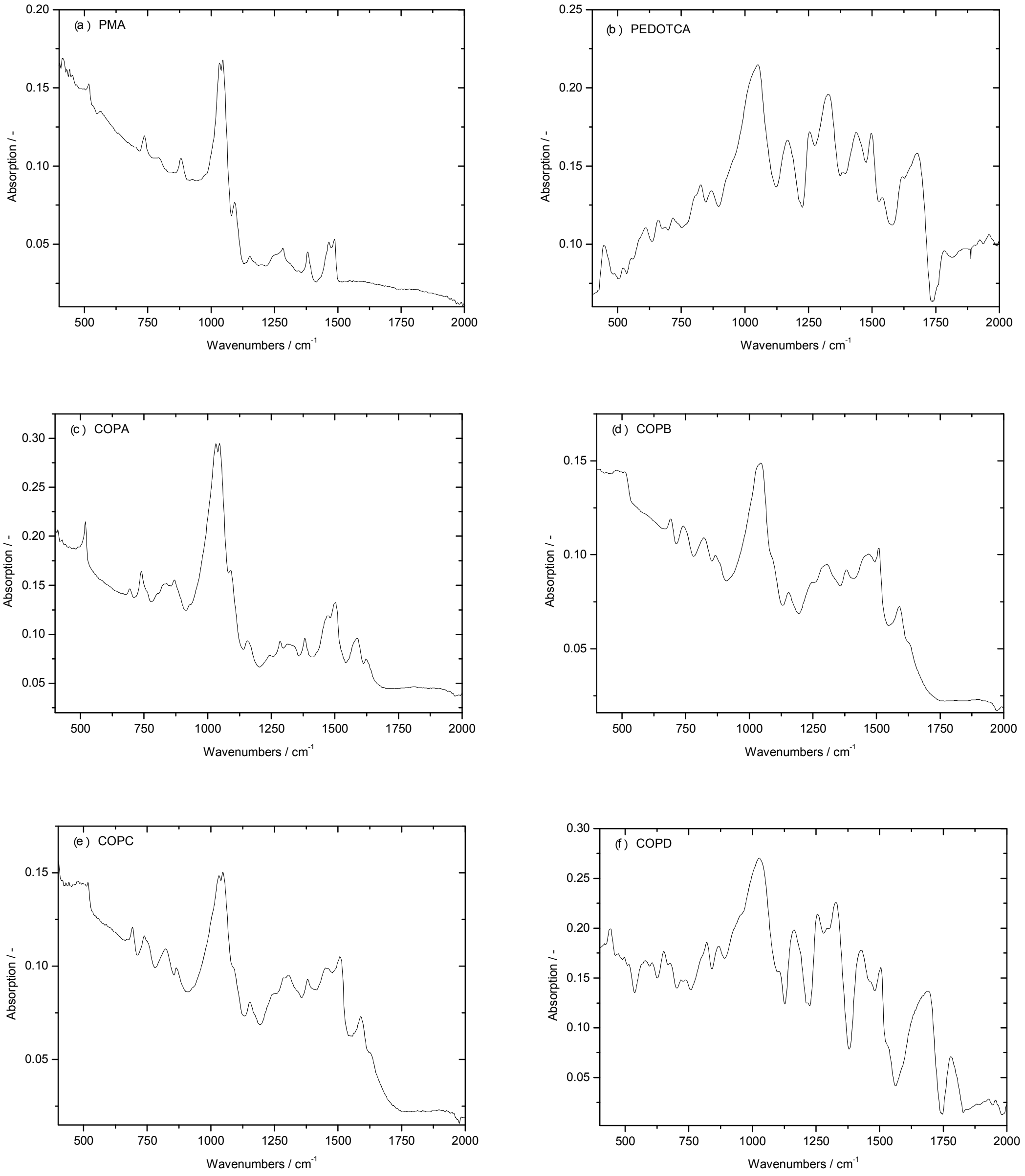

Figure 10. Infrared spectrum of the copolymers, resolution 4 cm^{-1}, 32 scans.

Table1. Assignment of vibrational modes of the homopolymers and copolymers.

Mode	Infrared Band Position (cm^{-1})					
	PMA	PEDOTCA	COPA	COPB	COPC	COPD
γ(ring)^{a}	412	-	413	-	-	-
β(C-(OH))^{b}	-	445	-	-	-	442
γ(ring)^{a}	499	-	-	478	-	-
n.a.	-	521	517	512	-	-
n.a.	561	-	-	-	-	578
n.a.	-	613	-	-	-	606
$\gamma_{as}(CH_2)^{b}$	-	659	-	-	-	651
n.a.	-	-	693	688	694	678
n.a.	-	716	-	-	-	714
γ(CH)^{a}	736	-	742	739	738	736
n.a.	791	-	-	-	-	-
$\beta_{as}(CH_2)^{b}$	-	820	837	822	823	821
ring breathing^{b}	-	865	866	867	863	862
γ(CH)^{a}	887	-	-	-	-	-
δ(ring)^{a}	1032	-	1029	-	1026	1024
ν(Ph-O-C)^{a}	1045	-	1047	1043	1044	-
ν(C-S)^{b}	-	1056		-	-	-
δ(CH)^{a}	1086	-	1092	-	-	1100
ν(C-N-C)^{a}	1150	-	1155	1157	1152	-
n.a.	-	1172	-	-	-	1173
ν(C-O-C)^{b}	-	1253	1242	1245	1242	1254
δ(ring)^{a}	1283	-	-	1292	1291	-
ν(ring)^{b}	-	1327	1326	-	-	1326
δ(CH)^{a}	1378	-	1379	1378	1382	-
ν(ring)^{b}	-	1430	-	-	-	1425
ν(ring)^{a}	1460	-	1468	1451	1453	-
ν(ring)a	1483	-	-	-	-	-
ν(ring)^{b}	-	1503	1504	1508	1505	1504
ν(ring)b	-	1536	-	-	-	-
n.a.	-	-	1585	1587	1584	-
ν(ring)^{b}	-	1619	1623	1623	1624	-
ν(C=O)^{b}	-	1674	-	-	-	1691
n.a.	-	1783	-	-	-	1776
n.a.	-	1923	-	-	-	1929
n.a.	-	1953	-	-	-	1956

^{a}: band corresponding to MA moiety of the polymer; ^{b}: band corresponding to EDOT moiety of the polymer; δ: in-plane deformation; γ: out-of-plane deformation; ν: stretchinz; β_{as}: rocking; γ_{as}: twisting; β: bend; n.a.: not assigned.

3.6 In situ conductivity measurements

The resistivity versus the applied electrode potential plot of PMA in 0.1 M TBATFB/acetonitrile is displayed in Figure 11a. PMA shows two changes in resistivity. When the applied potential is increased, the resistivity of PMA decreases sharply by 1.9 orders of magnitude at 0.15 V and then increases again at 0.69 V. When the potential shift is reversed from 1.0 to -0.2 V, the conductivity is almost completely restored. The resistivity versus the applied electrode potential plot of the other homopolymer, PEDOTCA in 0.1 M TBATFB/acetonitrile is displayed in Figure 11b. The polymer shows a single change in resistivity. When the applied potential is increased, the resistivity decreased sharply by 2.7 orders of magnitude around 0.49 V with a highly stable conductivity up to 1.2 V. In a potential scan back from 1.5 to -0.2 V, the resistivity is almost completely restored. The conductivity of PEDOTCA is around one order of magnitude lower than that of polythiophene (Vogel & Holze 2005). The high resistivity of polythiophene as compared to that of PEDOTCA should be related the structural difference between them. The presence of ethylenedioxy substituents at the thiophene ring in PEDOTCA increases the steric hindrance and distortion along the polymer chain which modifies the structure and thus the properties of the polymer. It should be mentioned that the observed conductivity of PMA is less than that of PEDOTCA by 2.1 orders of magnitude.

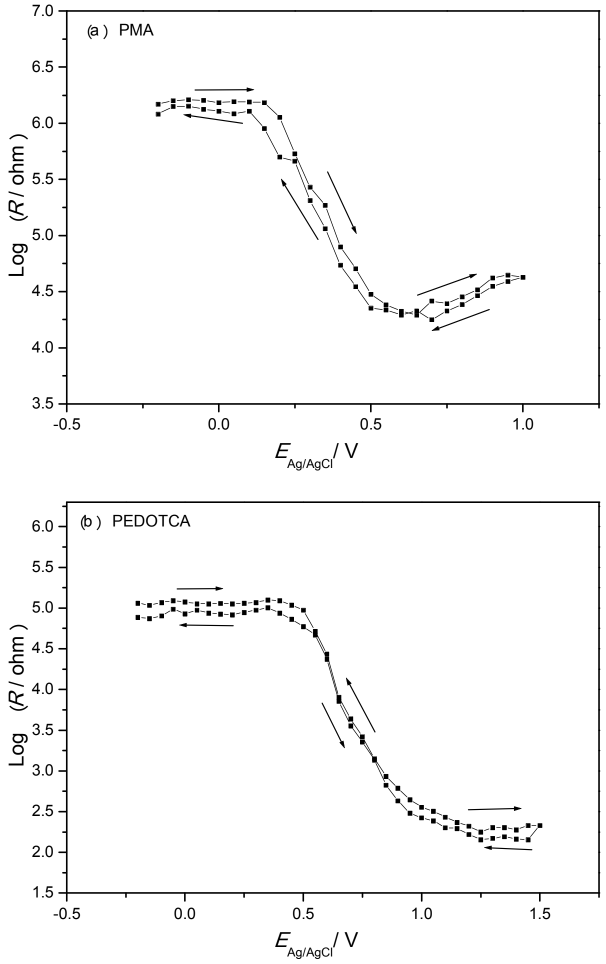

Figure 11. Resistivity versus electrode potential data in a solution of acetonitrile+0.1M TBATFB of (a) PMA, (b) PEDOTCA.

In situ conductivity measurements with different monomers concentrations in the polymerization solution were performed; results obtained with copolymers of different compositions are presented in Figure. 12a-d. The copolymer COPA (Figure. 12a) shows two change in resistivity. When the applied potential is increased, the resistivity decreases sharply by 2.1 orders of magnitude at 0.18 V with a stable resistivity up to 0.79 V and then increases again. The resistivity is almost completely restored when the potential is shifted back from 1.5 to -0.2 V. The conductivity behavior of this copolymer is very close to that of PMA and less than that of PEDOTC by 1.6 orders of magnitude. This indicates that high MA units are incorporated into the copolymer chains. The copolymers COPB (Figure. 12b) and COPC (Figure. 12c) show two change in resistivity. When the applied potential is increased, the resistivity decreases sharply by 2.2 orders of magnitude at 0.37 V in the case of COPB and by2.6 orders of magnitude at 0.46 V in the case of COPC. With further increasing the applied potential , the resistivity increased sharply at 0.88 V in the case of COPB and at 0.96 V in the case of COPC. The resistivity of COPB and COPC is not restored when the potential is reversed from 1.5 to -0.2 V. This might be due to degradation of these copolymers at high potentials. It was notable from the Figures 12b and c that the conductivity of the copolymers COPB and COPC is higher than that of PMA and less than that of PEDOCA. The conductivity of the COPD is observed to be 0.2 orders of magnitude less than that of PEDOT. From the Figure 12d, the resistivity of COPD is decreases sharply by 2.9 orders of magnitude at 0.48 V and with further increasing the applied potential , the resistivity increased at 0.95 V. The resistivity of this copolymer is not restored when the potential is reversed from 1.5 to -0.2 V. Based on the observations the in situ conductivity behaviors of the copolymers are not the sum of those of the two individual homopolymers, but seem to be determined by the EDOCA fraction in the copolymer. Figure 13 represents the minimum observed resistivity of the homopolymers and copolymers versus mole fraction of the EDOTCA that used in the polymerization solution. It was clearly that there is considerable drop in overall resistivity

even at the smallest EDOTCA-content.

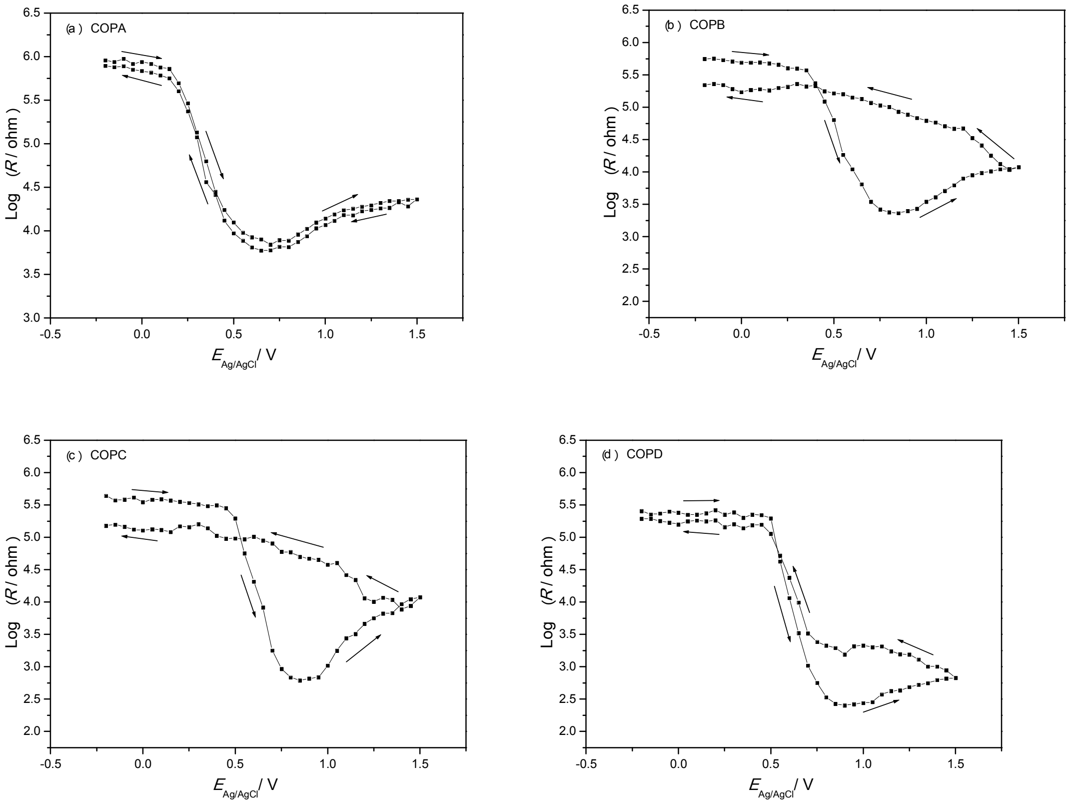

Figure 12. Resistivity versus electrode potential data in a solution of acetonitrile+0.1M TBATFB of (a) COOA, (b) COPB, (c) COPC, (d) COPD.

5. Conclusion

The electrochemical copolymerization of MA and EDOTCA was successfully realized in a non-aqueous electrolytes . At higher concentrations of MA in the feed, more MA units were incorporated into the copolymer. The copolymers showed fairly good stability. The copoly-mers formed with different feed concentrations of monomers exhibited different cyclic volt-ammetric behaviors. All in situ resistivities of the copolymers were higher than that of PMA in less than that of PEDOTCA homopolymers. Two transitions were observed in the in situ con-ductivities of the copolymers. A drop in overall resistivity of the copolymers was observed even at the smallest EDOTCA content.

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