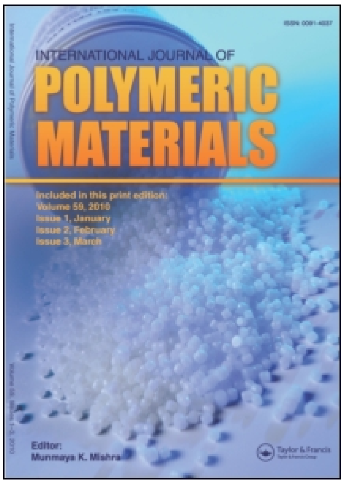

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AN ELECTROCHEMICAL STUDY OF SOLUBLE COPOLYMER OF ETHYL CARBAZOLE WITH N-METHYL PYRROLE AND 3-METHYL THIOPHENE

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AN ELECTROCHEMICAL STUDY OF SOLUBLE COPOLYMER OF ETHYL CARBAZOLE WITH N-METHYL PYRROLE AND 3-METHYL THIOPHENE

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Copolymers of N-ethyl Carbazole (ECZ) with N-Methyl Pyrrole (N-MPy) and 3-Methyl Thiophene (3-MTh) were synthesized on platinum substrate and electrochemical investigation of polymeric films was performed. The characterization of homopolymer and copolymer films was performed by electrochemical methods (i.e. polarization curves and cyclovoltammetric measurements), solid-state conductivity measurements and spectrophotometric methods comparatively. A possible scheme for the copolymerization has been suggested. Solid state conductivity of PECz can be improved by inclusion of 3MTh and NMPy into chain. The ionization potentials, I_p, electron affinity, E_a, optical band gap, E_g, peak potentials, E_p, and doping degrees, y, of copolymer electrodes were calculated from these measurements. Copolymer electrodes have lower I_p, E_g, E_p values and better switching properties in accordance with homopolymer electrodes. Presence of alkyl group gives solubility to copolymers obtained both chemically and electrochemically.

Keywords: N-ethycarbazole, N-methylpyrrole, 3-methythiophene, soluble copolymers

INTRODUCTION

Of all known conducting polymers, polypyrrole is the most frequently used due to its conductivity and the possibility of forming homopolymers, copolymers, or composites with optimal properties. But it is hard and brittle and these poor properties greatly restrict its potential for applications [1–3]. Attempts have been made for copolymerization of Py with other heterocyclic monomers with an aim of improving the

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properties of the resulting product. So far, copolymers of pyrrole with heterocyclic monomer have been prepared by electrolytic oxidation [4–6].

One of the problems involving conducting polymers is the difficulty of solubility in any solvent because of their delocalized p electronic structure, which is the very same molecular characteristic that gives rise to properties necessary for practical applications. It is possible to overcome this problem by structural modification or introducing matrix polymers to the reaction media [7–14]. In these cases the conducting polymer might lose some useful optical and electronic properties. Another way to obtain a soluble conducting polymer is copolymerization with a soluble macromonomer, which is expected to gain both conductivity and solubility from its respective two components [15]. When electronic properties are important, copolymerization starting from two conducting monomers that are substituted by alkyl group is more favorable.

Polymers containing N-alkyl-3-6-carbazole units were found to be soluble in organic solvents [16–19] and then easily processable. In our previous study we have reported the synthesis and electrochemical study of copolymer and composite electrodes of N-substituted carbazoles with pyrrole [5,6]. The results suggest that these electrodes have a possible application due to their stability and reversibility.

Alkylated polythiophenes (PATs) show good environmental stability and are soluble in common organic solvents when their alkyl group has at least 4 carbon atoms, hence these compounds have been extensively studied. Monosubstitution at 3-position of the ring introduces asymmetry to the monomer, allowing regioisomerism in the polymer [20].

Owing to these unique physical properties, polyconjugated soluble polymers are currently receiving considerable attention in the directions of clearer elucidation of structure-property relationships and the wide variety of their potential technological application [21–23]. Oxidative coupling of asymmetric 3-alkylthiophene by either electrochemical or chemical methods always results in a chain containing about 70–89 percent of head-to-tail (HT) configurational dyads, as determined by NMR analysis [24–25]. Due to this possibility of formation of regioregular polymers, 3-alkylthiophene was selected in this study.

Although preparation of soluble thiophene oligomers containing from three to 12 thiophene units or another conjugated monomer unit results in decrease of oxidation potential and idealized regularly α-linked polymers chain, it is a long and tedious work to study structure-properties relationship.

The electrochemical copolymerization of pyrrole and thiophene has been documented in the literature [26–29]. However, to our knowledge, copolymerization of alkyl substituted pyrrole and thiophene with ECZ with a goal of obtain we soluble polymers and improve we some electrochemical properties of polymer has not been reported so far.

In this paper, our attention has been directed to preparing a new soluble copolymer with short alkyl chain that does not have steric repulsion to twist the ring from coplanarity, which reduced the effective conjugation length. For this purpose ECZ was chosen to copolymerize with NMPy and 3-MTh as the internal conjugated moiety so as to provide a planar core, solubility and electrochromic properties.

EXPERIMENTAL

Materials

N-ethylcarbazole (ECZ) Aldrich >99%, N-methylpyrrole (NMPy) Merck >98% and 3-methylthiophene (3-MTh), Tetrabutylammoniumtetrafluoraborate, $TBABF_4$, dimethylformamide (DMF) and acetone (Ac) were employed. Acetonitrile (ACN) Carlo Erba was HPLC grade and the chemicals were all used as supplied. The prefix P indicates the corresponding polymer.

Electrodeposition and Measurements

Potentiodynamic electrodeposition was performed with a potentiostat Wenking POS 73 model in conjugation with X-Y recorder (Kipp and Zonen).

The nominal thickness was 40μ throughout to verify complete coating of the platinum and calculated electrochemically by using a Faraday equation as suggested in the literature [30]. Nominal thickness of the polymer layer can be calculated as follows:

$$d_n = (Q_0/2F\ A\ \rho)(m_1 + m_2 + m_A/N)$$

Q_0 = charge used for the synthesis in Coulombs, F = Faraday constant, ρ = density (1.2 g/l), m_1 = molecular weight of NMPy unit, m_2 = molecular weight of ECZ, m_A = molecular weight of anion doped. N = number of monomer units per anion and A is area of polymer in cm^2 .

Electrochemical experiments were carried out with a standard three-electrode cell. The working electrode was a Pt wire electrode ($A = 0.159\,cm^2$), which was cleaned by hot HNO_3 and H_2SO_4

ultrasonically. The counter electrode was Pt, and silver wire was selected as reference electrode. (The redox potential of ferrocene/ferrocenium couple was found to be 220 mV against this reference electrode.)

Preparation of Copolymers

Potentiodynamic electrodeposition of homopolymer of N-MPy and 3-MTh from ACN onto Pt were carried out as follows: The electrodes were first polarized from 0 mV up to 1.4 V and maintained for varying periods of time (300 s).

Copolymerization was performed in the same way as with a homopolymer in the presence of both monomers. From such experiments potentiodynamic electrodeposition (Q_0) and the first discharge ($Q_{E,0}$) in the background electrolyte (0.1 M Tetrabutylammoniumtetrafluoraborate, $TBABF_4$, in Acetonitrile) degree of doping, y, was calculated as suggested in literature [31].

$$y = 2\ Q_{E,0}/(Q_0 - Q_{E,0})$$

Doping degrees were 0.1, 0.4, 0.034 and 0.026, for PNMPy, P3MTh, P[NMPy-co-ECZ], P[3MTh-co-ECZ] polymers, respectively.

FT-IR measurements were performed with a Mattson 1000 spectrophotometer. Solid-state electrical conductivity measurements were performed from films removed from the electrode surface or pellets in the case of those chemically prepared on a Keithley 617 electrometer connected to a four probe head with gold tips and calculated from the following equation:

$$\sigma = V^{-1}\ I\ (\ln\ 2/\pi d_n)$$

where V is potential in volt, I is current in ampere and d_n is thickness in cm.

H-NMR spectra were obtained from the DMSO solution on a Bruker Ac (250 MHz) and the results obtained are as follows:

$$\mathbf{P[NMPy-co-ECZ]}\ \delta = 8.09\ (2H,\ d),\ 7.6-7.1(4H, m),\ 6.6\ (2H,\ dd),\ 6.1(H, d), 4.1-3.5\ (2H, q),\ 3.6(3H, s)\ 1.38(3H,\ s)$$

$$\mathbf{P[3MTh-co-ECZ]}\ \delta = 8.1\ (2H,\ d), 7.6-7.1(4H, m),\ 6.8\ (3H,\ dd),\ 4.1-3.5\ (2H, q), 2.3\ (3H, s),\ 1..3\ (3H, s)$$

RESULTS AND DISCUSSION

CV Results

Oxidation peak potentials (E_{pa}), corresponding reverse peak potential (E_{pc}), and onset potentials (E_{ox}), which are obtained from cyclic voltammogram of PNMPy, P[NMPy-co-ECZ], P3MTh, P[3MTh-co-ECZ], were summarized in Table 1. Ionization potentials (I_p) of homopolymer and copolymer electrodes were calculated as suggested in the literature [32–33]:

$$I_p = (E_{ox} + 4.4)\ \text{eV}$$

Redox properties of polymeric film depend on the voltage range of the prepared film. An increase of film thickness may block permeation of anions and hence increase reversible potential. In order to increase the response rate, the film thickness must be decreased, unlike our case, due to the requirement of high voltage that causes thicker film Dukida the formation of copolymers. For example, in the case of PNMPy, film that was prepared just beyond the oxidation potential of monomer (PNMPy [a], Table 1) has better properties than the film obtained at higher potential (PNMPy [b], Table 1). The E_{pa} values changed from 550 mV to 1000 mV as the film became thicker.

On the other hand, in order to obtain P[NMPy-co-ECZ] film, we should apply a suitable potential for both ECZ and NMPy, although this potential is higher than the oxidation potential of NMPy alone and application of such high potential results in thicker film. Similar results were obtained for P3MTh and P[NMPy-co-ECZ] copolymer film.

In the absence of direct measurements of reduction potential, it is a common practice to estimate electron affinity, E_a, by subtraction of

TABLE 1 E_{pa}, E_{pc}, E_{ox}, I_p, Eg, Ea, Values of Polymers (Polymer Film Obtained in the Range of −200 to 790* mV (a) and 0.0 to 1.2 V (b), *Film Formation Begins)

Polymer	E_{pa}(mV)	E_{pc}(mV)	Onset Pot. (E_{ox}') (mV)	I_p, eV (from CV)	E_g,eV (from UV)	E_a,eV
PNMPy(a)	550	490	− 100	4.30	–	–
PNMPy(b)	1000	850	500	4.90	2.48	2.42
P[NMPy-co-ECZ][b]	850	700	420	4.80	2.26	2.54
P3MTh[b]	800	650	380	4.78	1.88	2.90
P[3MTh-co-ECZ][b]	650	500	200	4.60	1.85	2.75

optical gap energy, E_g, from the I_p value determined either electrochemically or via other methods [32–33]. The optical gap obtained from absorption spectra is given in Table 1. From these data E_a values were estimated and are given in Table 1.

As can be seen from Table 1, the presence of ECZ in the PNMPy and P3MTh chain eases the electron transfer so that the ionization potential reduces. Oxidation potential of homopolymers and copolymers of 3MTh are lower than that of NMPy, resulting in a decrease in I_p and E_g values (Table 1).

Scan rate dependence was determined for all homopolymers and copolymers. As illustrated by Figure 1 for P[3MTh-co-ECZ], the current is linearly proportional to scan rate, indicating all electroactive sites are electrode supported.

Four probe conductivities of polymer are given in Table 2. Inclusion of 3-MTh and NMPy in the ECZ chain increases the conductivity, as expected. Conductivity of electrochemically prepared samples was measured from freestanding films, while the chemical ones were measured from pellets. The differences between chemically and electrochemically synthesized polymers result from preparation of samples as well as preparation method.

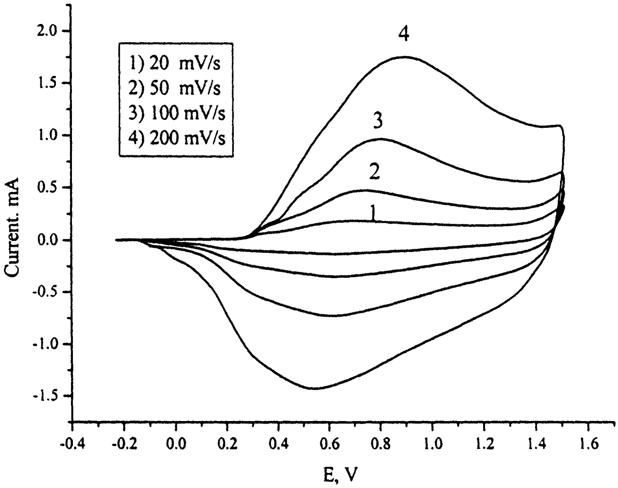


FIGURE 1 Scan rate dependence of cyclic voltammogram of P[3MTh-co-ECZ] electrochemically polymerized from mixture of 3MTh + ECZ at mol ratio of $n_{3MTh}/n_{ECZ} = 10$. 0.1 M $TBABF_4$/ACN solution using multiple (five cycles) cyclic voltammetry. Scan rates: 20 mV/s(1), 50 mV/s (2), 100 mV/s (3), 200 mV/s (4).

TABLE 2 Conductivity Values and Yields of Polymers

Polymer	Conductivity (S/cm) Chemical	Conductivity (S/cm) Electrochemical	Yields (g)
PNMPy	1.6×10^{-5}	$1.1\ 10^{-2}$	0.68
P[MPy-co-ECZ]	1.0×10^{-5}	$1.0\ 10^{-2}$	0.91
P3MTh	4.0×10^{-5}	$4.2\ 10^{-3}$	0.27
P[3MTh-co-ECZ]	3.0×10^{-5}	$1.0\ 10^{-4}$	0.89

On the other hand, the polymerization yields increase in comparison to homopolymers (Table 2). Together with conductivity values this result supports, the inclusion of ECZ in the polymer chain.

The relationship between onset potential (E_{ox}), ionization potential (I_p) and conductivity has a parallel trend (Figure 2). The conductivity of ECZ is lower than NMPy, 3-MTh, inclusion of ECZ in the polymer chain lowers the conductivity of copolymers. Since the conjugation still exists, the onset potential and ionization potentials are low for low conductivities (Figure 2).

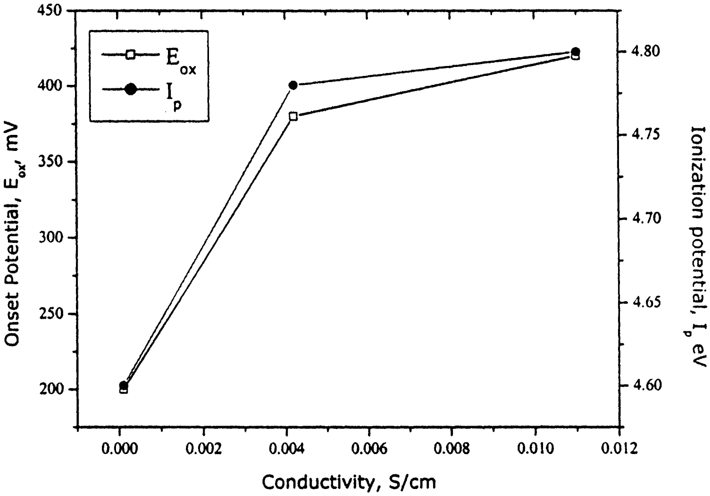


FIGURE 2 Relationship between the E_{ox}, I_p, and conductivity of homopolymer and copolymers.

Solubility of Polymers

Solubilities of polymers obtained electrochemically and chemically, which are followed by UV-visible measurements, are summarized in Table 3. Solubility of polymers in DMF is higher than in acetone. Inclusion of ECZ in polymer chain results in increase in solubility as expected.

The max absorbance values for polymers have red shift as compared to their monomers, as expected (Table 3). Increase in polarity of solvent results in a shift to lower energies. As can be seen from Table 3, the absorption spectra of copolymers are redshifted in both solvents, supporting the inclusion of ECZ in the polymer structure.

FT-IR Measurements

FT-IR spectra of PNMPy, P3MTh, P[MPy-co-ECZ], and P[3MTh-co-ECZ] were obtained and the positions of absorption bands in each spectrum are listed in Table 4, and given in Figure 3. The presence of 1322 cm^{-1} band due to C-CH_3 bending of ECZ testifies to the inclusion of ECZ in the PNMPy chain and that the pendant ethyl groups remained unaltered. The most characteristic difference in the copolymer is the lack of inter band at 1322 cm^{-1}, which is characteristic of oxidized PTh's [34–35], although the absorption band at 1100 cm^{-1}, which is known to appear at both oxidized PNMPy and P3MTh, is seen from this copolymer.

The absence of band around 1322 cm^{-1} for the copolymer strongly suggests that isolated P3MTh chains do not eventually exist in the copolymer and ECZ and P3MTh monomers are bonded effectively during polymerization.

TABLE 3 Solubility and λ_{max} Values of Polymers in DMF and Acetone (t = 25 C)

	Solubility (g/mL)		λ_{max}	
Polymer	DMF	Acetone	DMF	Acetone
PNMPy	0.005	0.015	277	336
P[MPy-co-ECZ]*	0.009	0.019	293	339
P3MTh	0.030	0.017	284	334
P[3MTh-co-ECZ]*	0.030	0.030	302	340
MPy	0.030	0.030	–	330
3MTh	0.030	0.030	–	310

* polymers obtained both electrochemically and chemically

TABLE 4 FT-IR Results

Polymer	Band Position of FT-IR spectra (cm^{-1})						
PNMPy	1620	1510	1440		1100		620
P[MPy-co-ECZ]	1661	1389	1322		1100	869	620
P3MTh	1620	1510	1440	1270	1100		620
P[M3Th-co-CZ]	1660	1550	1400	1250	1100		620

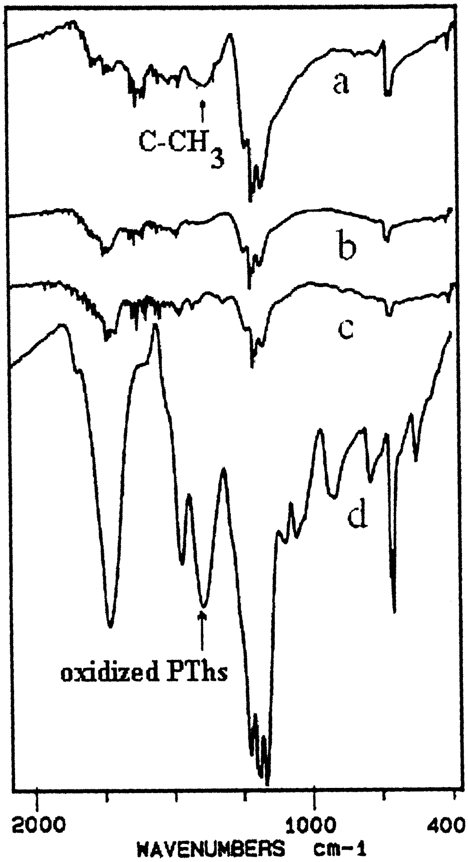


FIGURE 3 FT-IR spectra of P[NMPy-co-ECZ] (a), PNMPy (b), P[3MTh-co-ECZ] (c), and P3MTh (d).

Optical Properties

Spectroelectrochemical methods were also employed to study the changes in band position of polymers during oxidation (p-doping). Polymer films for spectroelectrochemical analysis were electrochemically polymerized on ITO glass and subsequently washed with ACN and placed in a quartz cuvette with counter and reference electrodes. The polymers were reduced to a neutral state by applying negative voltage at −1.0 V.

An example obtained by in-situ measurements is given in Figure 4, where three peaks were observed at three different wavelengths that are $\pi \rightarrow \pi^*$ transition at 302 nm, polaron at 450 nm and bipolaron at 850 nm, for the oxidized state of PNMPy. As the polymer reduces the absorption peaks around 450 nm and 850 nm decrease, which is consistent with the disappearance of cationic charge carriers while the peak at 302 nm increases. During this reduction, the color of polymer film changes from dark green to yellowish. In these conditions, although the polymeric film is reversible, switching time is not sufficient for applications.

In the case of ECZ, the formation of only soluble species, which diffuse through the solution, limits the investigation of the redox properties of homopolymer of ECZ film in the manner shown above.

The UV-visible spectrum of oxidized (1) and neutral (2) form of copolymer film of P[MPy-co-ECZ] obtained at mol ratio of $n_{MPy}/n_{ECZ} = ½$ is given in Figure 5. Reversibility of this film seems better than that of

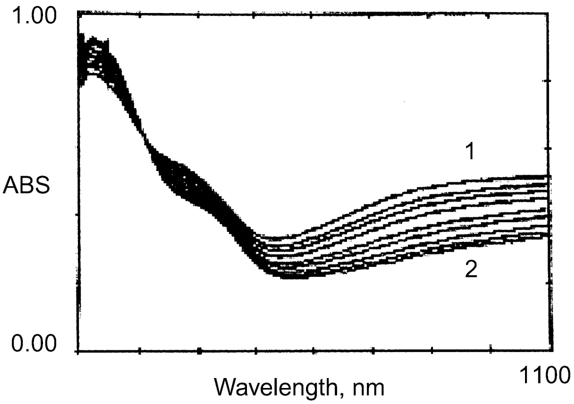


FIGURE 4 UV-visible absorption spectra of oxidized (1) and neutral that was obtained by reduction at −1.0 V for 30 sec (2) PNMPy film on ITO (other spectra between 1 and 2 obtained during reduction of film at every 30 sec).

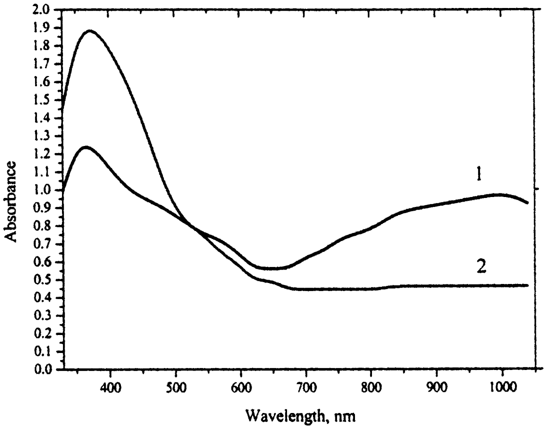


FIGURE 5 UV-visible absorption spectra of oxidized (1) and neutral that was obtained by reduction −1.0 V for 30 sec (2) P[NMPy-co-ECZ] film on ITO.

this homopolymer due to the electrochromic properties of ECZ. Reoxidation of film results in a decrease in the absorption peak at 345 nm with the appearance of a new broad peak beyond 700 nm, which is attributed to formation of delocalized cationic charge carriers. Switching properties of copolymer film obtained at the mole ratio of $n_{MPy}/n_{ECZ} = 1$ were found to be not as good as the copolymer film obtained at the former ratio, which might be due to the advantage of presence of ECZ in the chain.

Figure 6 shows the absorption spectra of P3PTh film (solid lines). The absorbances for oxidized form (1) beyond 700 nm decrease and a new peak at 500 nm occurs and the color of polymer film changes from dark blue to reddish as it is reduced (2).

Similarly to PNMPy, inclusion of ECZ in the P3MTh structure positively affects the redox properties of polymer. As can be seen from Figure 6, the copolymer film (dashed lines) has better switching properties.

Spectroelectrochemical Measurements

In order to investigate the reaction in solution, the next experiment was carried out with a 0.1 M 3-MTh solution that electrolyzed at 1.6 V for 1 h. After that period the variation in absorbance at $\lambda = 533$ nm with time was obtained by UV-visible spectrophotometer. To the electrolyzed 3 MTh solution the same concentration ECZ was added in one portion and variation of absorbance changes were followed in a similar

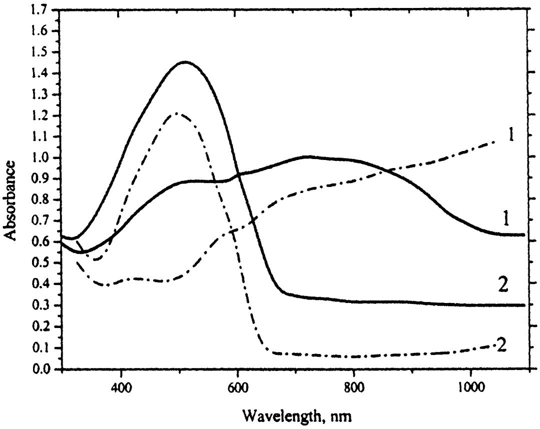
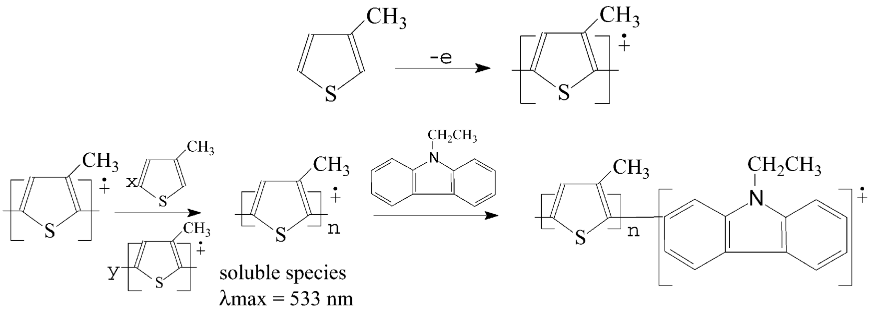


FIGURE 6 UV-visible absorption spectra of oxidized (1) and neutral that was obtained by reduction −1.0 V for 30 sec (2) P3MTh film (solid line) and P[3MTh-co-ECZ] film (dashed line) on ITO.

way. Results are show in Figure 7. Decrease in absorbance in the presence of ECZ is higher than the 3MTh solution alone. This result indicates that oxidized 3MTh species might react with ECZ monomer to produce a copolymer (Scheme 1).

During the PNMPy formation on ITO electrode, which is, followed by UV-visible measurements, max absorbance around 450 nm, attributed to the formation of polarons, disappeared in the presence of ECZ at the same conditions. This result supports the reaction between polarons of NMPy with ECZ. The same results were observed in the case of 3MTh. Maximum absorbance at $\lambda = 540$ nm disappeared in the presence of ECZ.



SCHEME 1 Mechanism of electrocopolymerization.

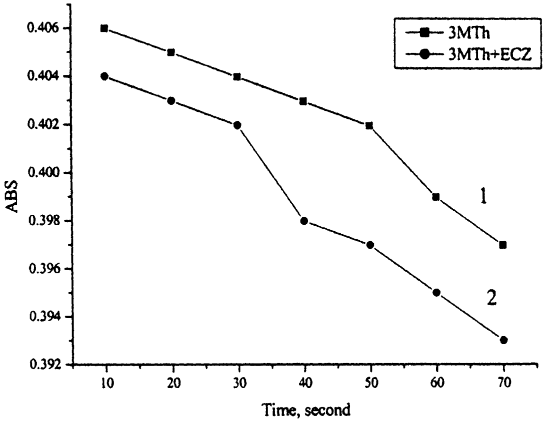


FIGURE 7 Variation of maximum absorbance (at $\lambda = 533$ nm) of electrolyzed 0.01 M 3MTh in the absence (1) and presence (2) of 0.001 M ECZ with time.

Together, the results of the measurements in solution (Figure 7) support the conclusion that the oligomeric species react with the other monomer during the copolymer formation.

CONCLUSION

We have shown that copolymers of N-etylcarbazole with N-methyl pyrrole and 3-methylthiophene can be prepared and they are soluble in DMF to some extent, which allows us to characterize the polymers with conventional techniques such as NMR and spectrophotometry. The cyclic voltammogram of these electrodes suggests that peak values shift to higher potentials with film thickness. In this study, differently from literature, I_p, E_g, E_a, values were first calculated for such copolymers. Although higher peak potentials were observed, copolymerization eases the electron transfer so that it reduces the I_p and E_g values as well as giving better reversibility and switching properties to this films.

The increase in conductivity in accordance with PECZ is therefore suggested to result from formation of copolymer film, since the conductivity of PECZ is known to be lower than both PNMPy and P3MTh.

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