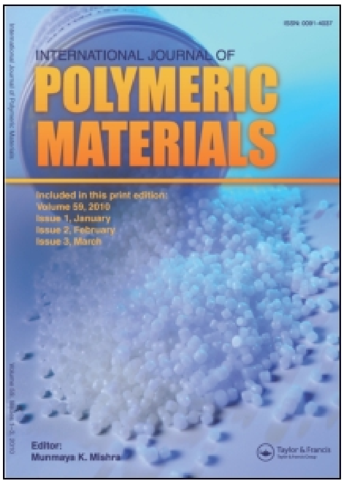

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# CONTROLLED ELECTROCOPOLYMERIZATION OF THIOPHENE WITH N-ETHYL CARBAZOLE: IN-SITU AND EX-SITU SPECTROELECTROCHEMICAL INVESTIGATION AND CONDUCTIVITY RELATIONSHIP

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# CONTROLLED ELECTROCOPOLYMERIZATION OF THIOPHENE WITH N-ETHYL CARBAZOLE: IN-SITU AND EX-SITU SPECTROELECTROCHEMICAL INVESTIGATION AND CONDUCTIVITY RELATIONSHIP

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*Polymerization of thiophene (Th) was studied in the presence of N-ethyl carbazole (ECz) by in-situ and ex-situ spectroelectrochemical measurements. In-situ spectroelectrochemical measurements allow determining some soluble thiophene oligomers. Cooligomeric species of Th-ECz (which give peaks at 376, 400 nm) are in parallel line with the findings from CV measurements (current values of peaks of electrogrowth of polymer). Results also suggest that ethylcarbazole and thiophene react on the electrode surface as well as in solution, and the percentage of ECz incorporated into the polymer structure is less than in the case of the electrode surface reaction.*

*CV's of PECz, PTh and P [Th-co-ECz] formation indicate shifts in $E_p$ and corresponding current changes. Increase in peak currents intensities of ECz in the presence of Th, $I_{p1}$ for ECz, Th, [Th-co-ECz] is 0.05 mA, 1.6 mA, 2.0 mA, respectively, giving a ratio of 1/32/40 ($I_{p1}$) and 1/9/21 ($I_{p2}$) supporting the inclusion of ECz into copolymer structure. The conductivities of PTh and copolymer-measured by four-point-probe technique (at mole ratio of $n_{Th}/n_{Ecz} = 25$) were found as 42 mS/cm and 36 mS/cm, respectively, giving a ratio of 42/36 = 1.67, which is in line with $I_p$ values of electro growth of copolymer on the Pt [i.e., for ratios of P[Th-co-Ecz]/PTh of $I_{p1}$ 40/32 = 1.3 and for $I_{p2}$ = 21/9 = 2.3].*

**Keywords:** thiophene, N-ethylcarbazole, copolymer, electropolymerization

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## INTRODUCTION

Polythiophenes have shown considerable promise for materials applications due to their unique electrical properties and their environmental stability [1–4]. However, the high oxidation potential of thiophene compared to the polymer causes some degradation of the polymeric film, a subject of several studies. Recently, this problem was overcome by extending the conjugation length of the monomer, resulting in a significant reduction in the oxidation potentials [5–10]. In our previous study, we have synthesized and polymerized some ter-arenes based on N-ethylcarbazole and thiophene [11]. N-ethylcarbazole was chosen as an internal conjugated moiety so as to provide a planar, synthetically flexible core, which could easily be derivatized with no loss in extent of conjugation [5] or solubility due to its alkyl group. Since the yield of synthesis is very low, it was a tedious and expensive way to investigate the structure and mechanism of polymerization. Instead of this we try to gain further information by in-situ spectroelectrochemical measurements from the mixture of two monomers at suitable ratios.

Within the past decade, various carbazole derivatives have been studied for their suitability for electroluminescent devices [12–34].

There is no coherent film bound to the anode substrate during the oxidation of N-ethylcarbazole and N-phenyl carbazoles in acetonitrile solution [13, 33]. Introducing Th moieties into polymer structure may result in a stable and coherent polymeric film having the properties of both monomers.

Although soluble, thiophene oligomers containing from three to twelve thiophene units or other conjugated monomer units result in decreased oxidation potentials and idealized regularly $\alpha$-linked polymer chain. Their synthesis is a long and tedious work.

In this study it was aimed to investigate the mechanism and structure of thiophene polymerization during the introduction of another conjugated monomer such as ECz. For this purpose, controlled electropolymerization of Th with ECz, which itself does not electropolymerize under these conditions, was performed.

The results indicated that a combined method for following the electrocopolymerization of Th and ECz in well-defined spectroelectrochemical conditions results in increase–conductivity and/or physical properties of the product, as expected.

## EXPERIMENTAL

Thiophene (Th) and N-ethylcarbazole (ECz) were obtained from Aldrich Chemical Company and used without further purification.

A Wenking POS 73 Model scanning potentiostat connected with a Kipp and Zonen X-Y Recorder was employed for electrochemical measurements. Constant potential electrolysis was performed in HPLC grade acetonitrile (ACN) containing 0.2 M $NaClO_4$ supporting electrolyte by using Pt and indium tin oxide (ITO) as a working electrode, Ag/AgCl covered Ag wire as a reference electrode and Pt as a counter electrode. In-situ spectroelectrochemical measurements were carried out in the range of 0.0−1.8 V.

A Shimadzu 160 UV-Visible spectrophotometer was used both for in-situ and ex-situ spectroelectrochemical measurements. FT-IR measurements were performed by a Mattson 1000 FT-IR spectrophotometer.

Solid-state conductivity measurements were performed on films removed from an electrode surface with a Keithley 617 electrometer connected to a four-probe head with gold tips.

## RESULTS AND DISCUSSION

Since the oxidation potentials of the two monomers, Th and ECz, are quite different from each other, polarization curves of ECz, Th and ECz + Th mixture were obtained in order to determine the proper ratios that allow the copolymerization by oxidation of ECz under limiting diffusion control conditions (Figure 1) at a potential where thiophene oxidation takes place. The polarization curve of Th (A) and ECz (B) almost add up to make the polarization curve of mixture (C), suggesting that copolymerization occurs at the given conditions.

The cyclic voltammogram in Figure 2 shows that ECz system has two anodic peaks, one at the higher potential belongs to oxidation of monomer and the other at the more cathodic value attributed to the oxidation of 3, 3′ dicarbazyl, as suggested in the literature [13, 33].

Oxidation of Th on an electrode surface takes place at about 1470 mV vs. Ag/AgCl (Figure 3A). The resulting radical cation encounters another radical monomer or oligomer [3, 4]. Alternatively, the radical cation reacts with a neutral monomer molecule and two $\alpha$-hydrogen atoms are then split off as protons. This process is repeated. At the same time, the polymer chains are also oxidized and reach electroneutrality by the inclusion of the counter ion from the electrolyte. The formation of polymeric films can be followed by the increase in current densities upon repetitive cycling. The polymeric film of Th has an anodic peak at 0.82 V and corresponding cathodic peak at 0.64 V in background electrolyte (Figure 3B).

In the presence of ECz, the cyclic voltammogram of Th becomes completely different from the CV of Th alone. (Figure 4A). The heights

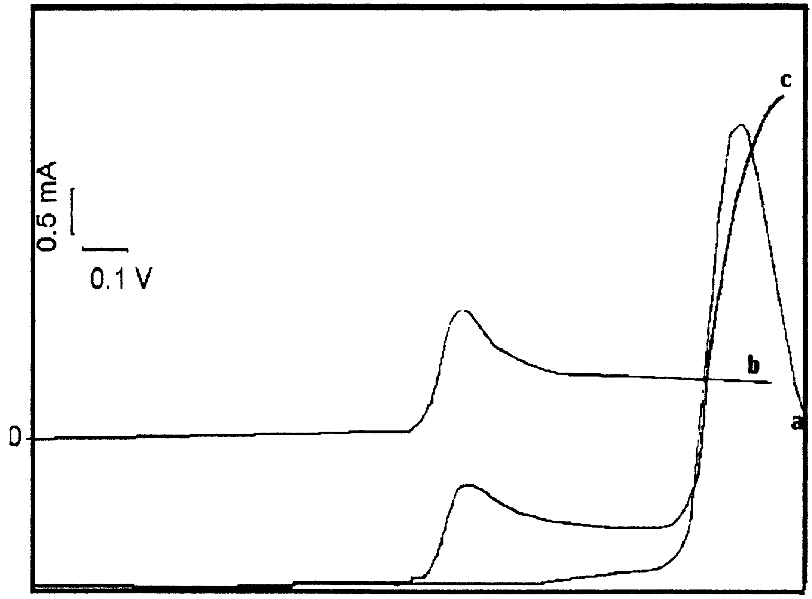


**FIGURE 1** Anodic polarization curves of 0.130 M Th (a), $4.0 \times 10^{-3}$ M ECz (b) and a mixture of both species in above described concentration (c) on Pt electrodes in ACN containing 0.2 M $NaClO_4$. Scan rate 50 mV.s$^{-1}$.

of anodic peaks at potentials around 700 mV and 1070 mV increase with increasing scan number, showing that a deposition of polymeric film on the electrode surface occurs. In our previous study [11] similar peaks (at 0.848 and 1.21 V vs. Fc/Fc$^+$ redox couple) have also been observed in the CV of ECz-Th comonomer. These two results show that ECz is incorporated into the polymeric film. Although ECz alone does not produce a film on the electrode surface, in the presence of Th a polymeric film having an anodic peak at 750 mV and a cathodic peak at 680 mV, both of which are lower than the peak values of PTh alone, support the same idea (Figure 4B).

Difference of the shapes of CV of ECZ (Figure 2), Th (Figure 3), and Th + ECZ is very distinct. ECZ gives two relatively reversible peaks at $E_{p1} = 0.7$ V, $E_{p2} = 0.99$ V. Anodic polarization of Th exhibits one peak at $E_{p1} = 0.82$ V and a reverse peak at $E_{p1} = 0.8$ V. On the other hand, P[Th-co-ECZ] shows peaks at $E_{p1} = 0.7$ V and $E_{p2} = 1.07$ V without a reverse peak, which could be an explanation of fast chemical step.

$I_{p1}$ for ECz, Th and [Th-co-ECz] is 0.05 mA, 1.6 mA, 2.0 mA, respectively, giving a ratio of 1/32/40 and indicating the inclusion of ECz into Th structure, in addition to the consideration of the shifts

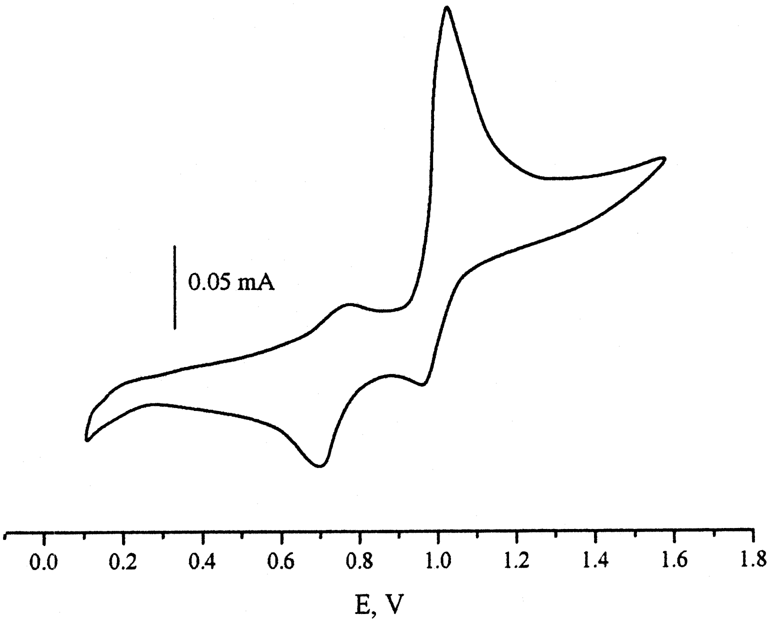


**FIGURE 2** Cyclic voltammogram of $1.0 \times 10^{-2}$ M ECz in ACN containing 0.2 M $NaClO_4$. Scan rate 100 mV.s $^{-1}$.

and disappearance of corresponding peaks in the copolymer. Similar comparison for $I_{p2}$ for ECz: Th: [Th-co-ECz] is about 0.18 mA/ 1.6 mA/3.75 mA with a ratio of 1/9 /21.

The conductivities of PTh and copolymer—measured by four point-probe technique (at mole ratio of $n_{Th}/n_{Ecz} = 25$)—were found as 42 mS/cm and 36 mS/cm, respectively, giving a ratio of $42/36 = 1.67$. The current ratios (for $I_{p1}$) give almost the same ratios ($40/32 = 1.3$). Solid state conductivity of PECz obtained in different media or chemically in acetonitrile varies in the range of $10^{-3}$–$10^{-5}$ S cm $^{-1}$ [33, 34].

One can suggest that without estimate of copolymers' surface coverage (relative thickness), the larger current observed cannot be used to infer that one polymer is more conducting than the other. However, when solid state conductivity values and peak currents are compared with feedstock ratios it is possible to reach the same conclusion (Figure 5).

The increase in current of copolymer is consistent with the finding in absorbance versus current values.

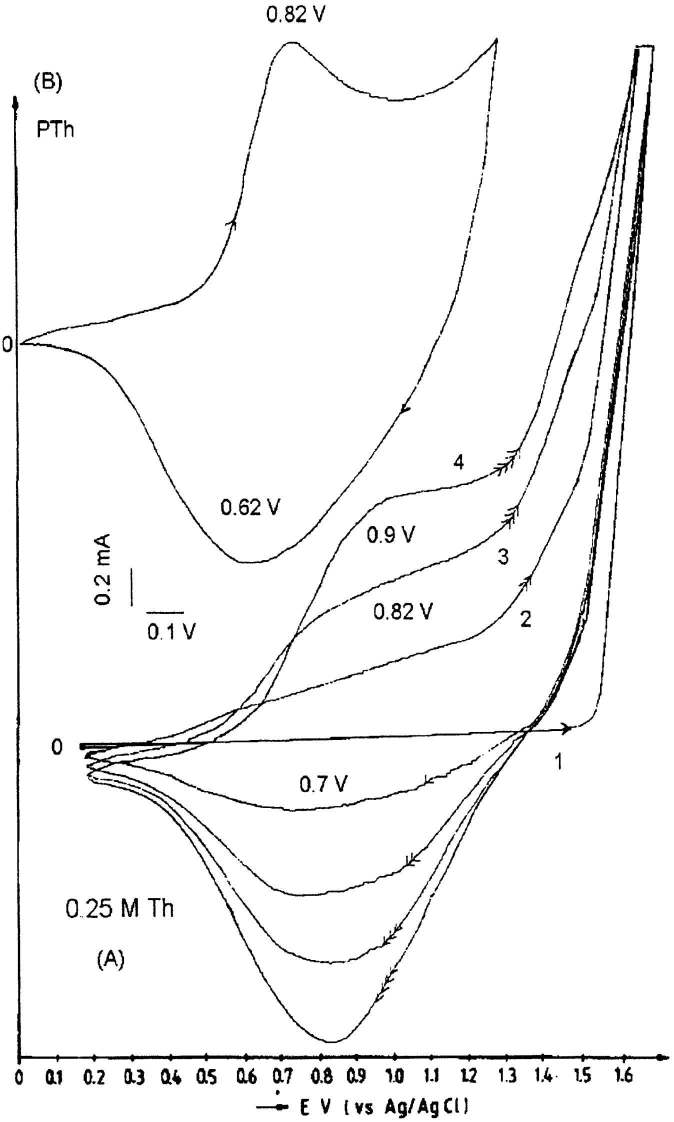


**FIGURE 3** Cyclic voltammogram of 0.25 M Th (A) (1,2,3,4 represent the number of cycle) and PTh film (B) in acetonitrile containing 0.2 M $NaClO_4$. Scan rate 100 mV.s $^{-1}$.

The UV-visible spectra of the polymeric films were measured by growing them on an indium tin oxide (ITO) surface (Figure 6, curve 1 and 2). PTh film has two main peaks around $\lambda = 415$ nm and

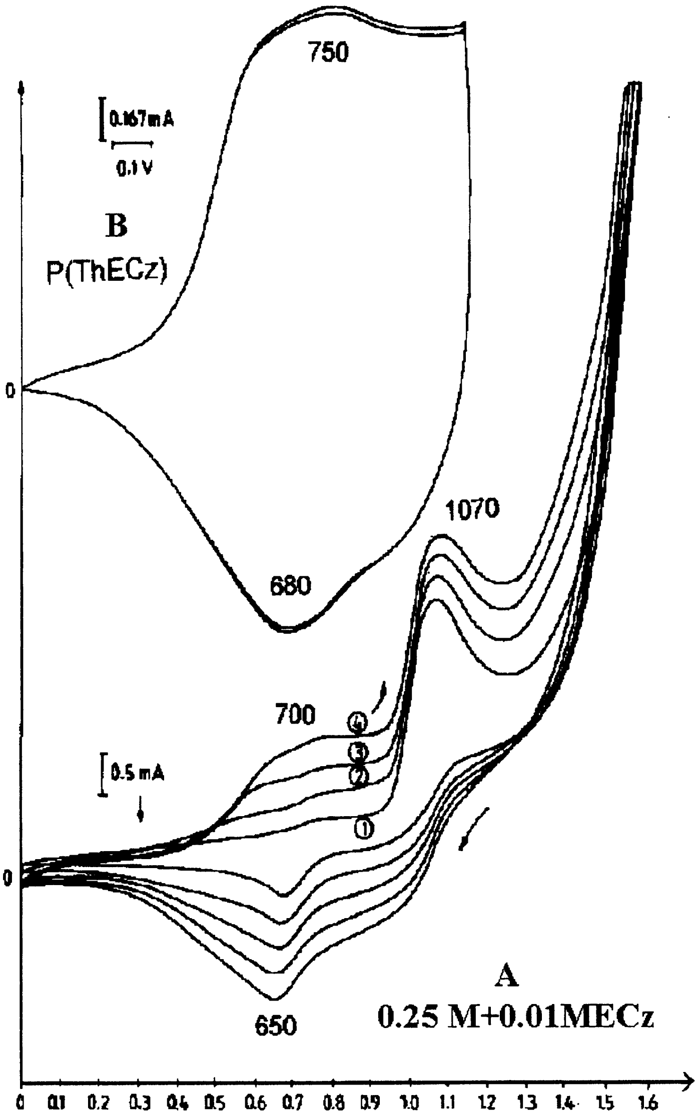


**FIGURE 4** Cyclic voltammogram of mixture of 0.25 M Th and 0.01 M ECz (A) and polymeric film obtained in this conditions (B) in ACN containing 0.2 M $NaClO_4$. Scan rate 100 $mV.s^{-1}$.

$\lambda = 810$ nm (Figure 6, curve 1). In the presence ECz (at mole ratio of $n_{Th}/n_{Ecz} = 25$) the presence of characteristic band of polycarbazole derivatives [35, 36] proves the incorporation of ECz into copolymer

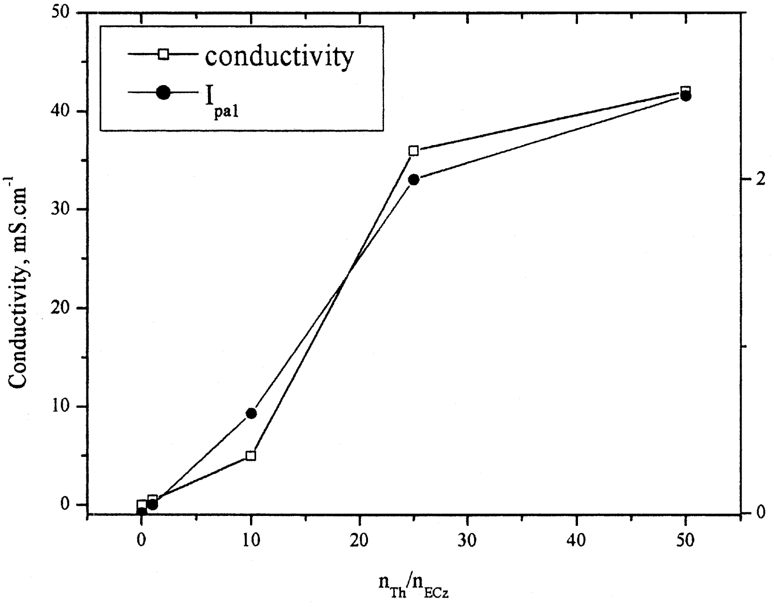


**FIGURE 5** Variation of solid state conductivity values of copolymers depending on feedstock ratios.

structure (Figure 6, curve 2). The polythiophene character became dominant by increasing the Th percentage, and vice versa, as expected.

The FT-IR spectra of copolymer and PTh are shown in Figure 7a and b, respectively. The most significant difference in the copolymer is the decrease in the intensity of the band at 1340 cm$^{-1}$, which is characteristic of oxidized PTh [37–39]. The band at 1100 cm$^{-1}$, due to the incorporation of $ClO_4^-$ ions [18], appeared in both PTh and copolymer (Figure 7a and b). Another noticeable feature in the spectrum is the absorption band around 790 cm$^{-1}$, which indicates polymerization through the α-position of each monomer.

The formation and growth of the polymer films on platinum electrodes from the solution was followed by gravimetric determination of the polymer grafted on the electrode, as suggested in the literature [40]. Kinetic parameters suggested the formation of a copolymer structure on the electrode surface.

The in-situ UV-visible spectrum of 0.13 M Th, and the variation of the maximum absorbances with time, are given in Figure 8. The presence of a maximum at $\lambda = 328$ nm suggests the formation of bithiophene during the polymerization as expected, and the maximum

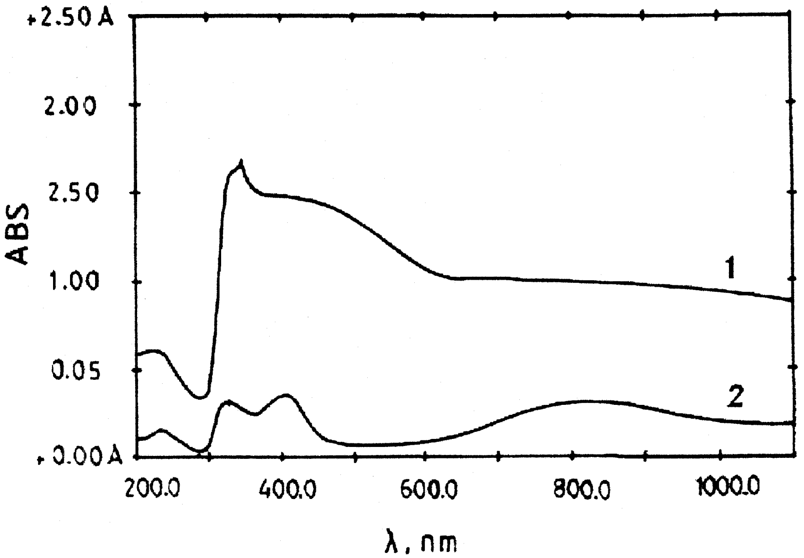


**FIGURE 6** UV-visible spectra of and copolymer film obtained on ITO surface from a mixture of and 0.25 M Th + $7.0 \times 10^{-3}$ M ECz (1), 0.13 M Th and $2.6 \times 10^{-2}$ ECz (2).

at higher wavelengths corresponds to higher oligomers of thiophene. Only in-situ UV-visible measurements allow us to determine these intermediates. During ex-situ UV-visible measurements only a maximum at $\lambda = 659$ nm was observed.

In the in-situ UV-visible spectrum of 0.002 M ECz, four main peaks were observed at $\lambda = 376$ nm, 402 nm, 506 nm and 800 nm. While the absorbance values at $\lambda = 376$ nm and 402 nm increase with reaction time, variation of absorbance values at $\lambda = 506$ nm and 800 nm with time shows minima and maxima (Figure 9). It is interesting to observe that while the absorbance values at $\lambda = 800$ nm, corresponding to cation radicals of ECz and its oligomers, decreases, the values at $\lambda = 506$ nm increase. This result suggests that the peak at shorter wavelength ($\lambda = 506$ nm) might correspond to neutral intermediates resulting from the coupling reactions of cation radicals observed at $\lambda = 800$ nm.

In the mixture of Th (0.13 M) and ECz (0.002 M) three peaks that are also observed in the case of ECz alone were determined regardless of the monomers feed ratio. At the beginning of measurements there were three other peaks at $\lambda = 586$ nm, $\lambda = 660$ nm, $\lambda = 595$ nm. However, they disappeared in 10 minutes. When Th was oxidized, a peak

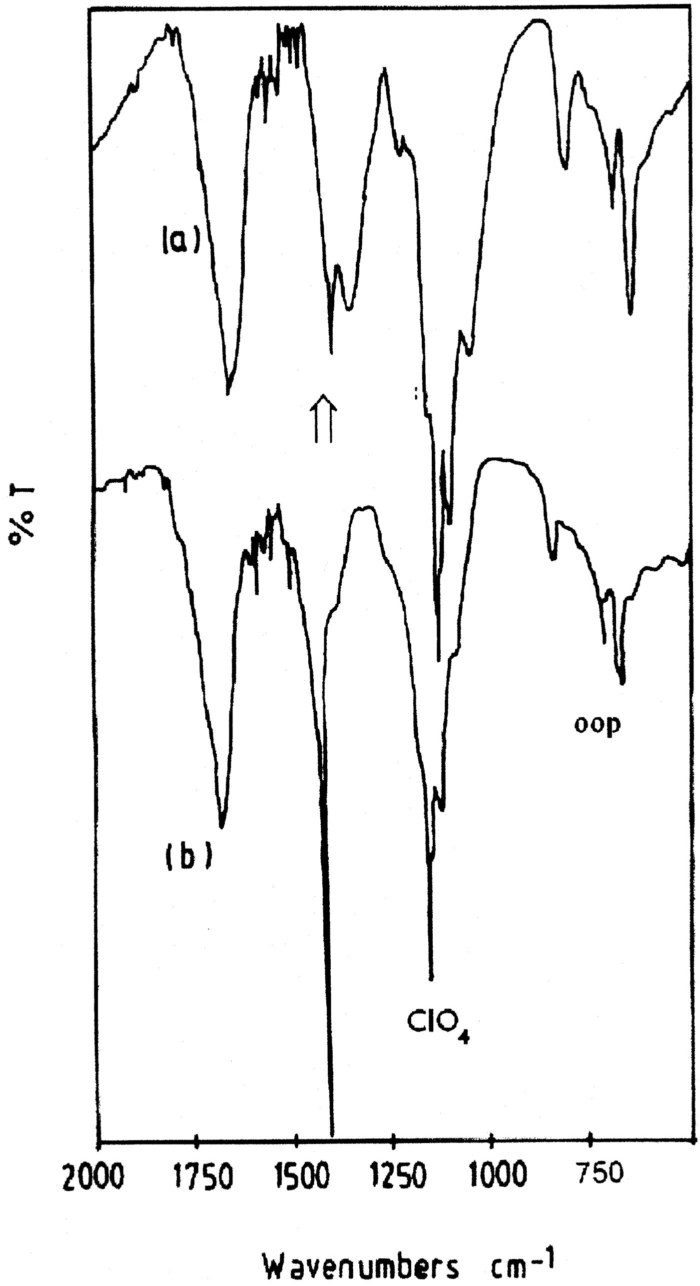


**FIGURE 7** FT-IR spectra of copolymer film obtained from a mixture of 0.13 M Th + $5.0 \times 10^{-3}$ M ECz (a) and PTh (b) obtained at the same concentration (0.13 M Th).

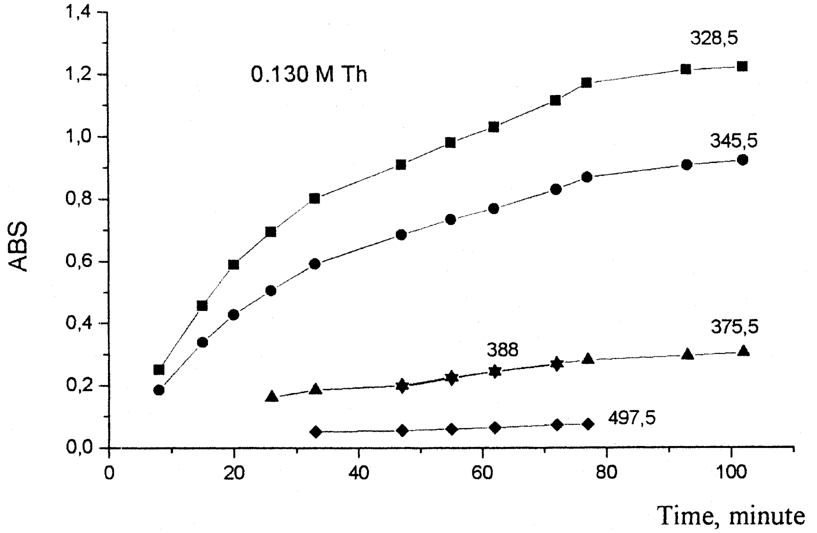


**FIGURE 8** Variation of UV-visible peak absorbances of 0.13 M Th during in-situ cyclic voltametric measurements in the range of 0.0–1.8 V vs. Ag/AgCl with time.

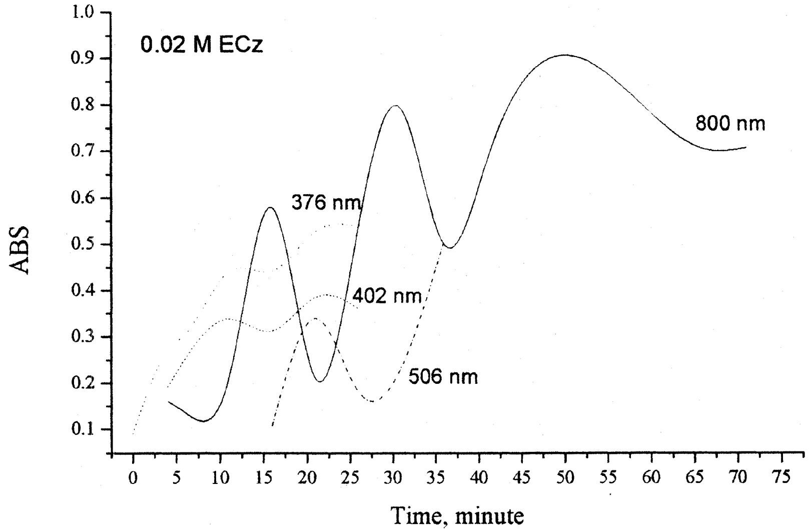


**FIGURE 9** Variation of peak absorbances with time during the cyclic voltametric measurements of $2.0 \times 10^{-2}$ M ECz.

at $\lambda = 659$ nm was observed. So the peak at this wavelength observed during in-situ measurement corresponds to the oxidized form of Th and its oligomers, and its disappearance suggests the reaction between these oligomers and ECz.

In order to understand the reaction between Th and ECz, ex-situ spectrophotometric measurements were also carried out. When Th was electrolyzed for 90 seconds, a blue solution having a peak at $\lambda = 659$ nm was observed as mentioned before. The other peaks that were observed during in-situ measurement could not be determined in this case. The absorbance values of the peak ($\lambda = 659$ nm) decrease with time, suggesting that coupling reactions are occurring (Figure 10a, curve ■). When ECz was added to this solution, the absorbance values decreased more rapidly than with Th alone, suggesting that cation radicals of Th react with ECz monomer (Figure 10a, curve ●). From the slopes of these curves of a ratio initial reaction rates of 1.6 for Th/(Th + ECz) was obtained, meaning that the addition of 0.02 M ECz accelerates the rate by a factor of 1.6.

When ECz was oxidized for 90 seconds a green–colored solution having a peak at $\lambda = 811$ nm was observed. The absorbance values of this solution could only be measured after one hour since they were so high and decreased with time (Figure 10b, curve ●). When Th monomer was added to this solution the absorbance value decreased

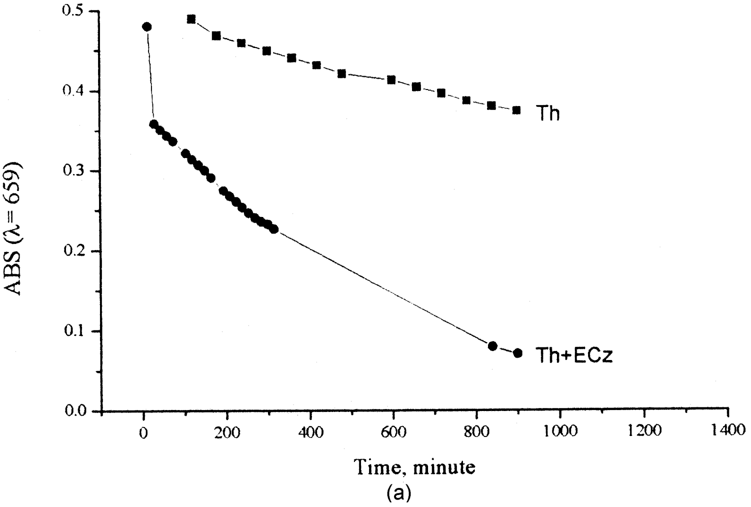


**FIGURE 10a** Variation of peak absorbance (at $\lambda = 659$ nm) values of the solution obtained by 90 seconds oxidation of 0.25 M Th (■) and after the addition of $2.0 \times 10^{-2}$ M ECz (●).

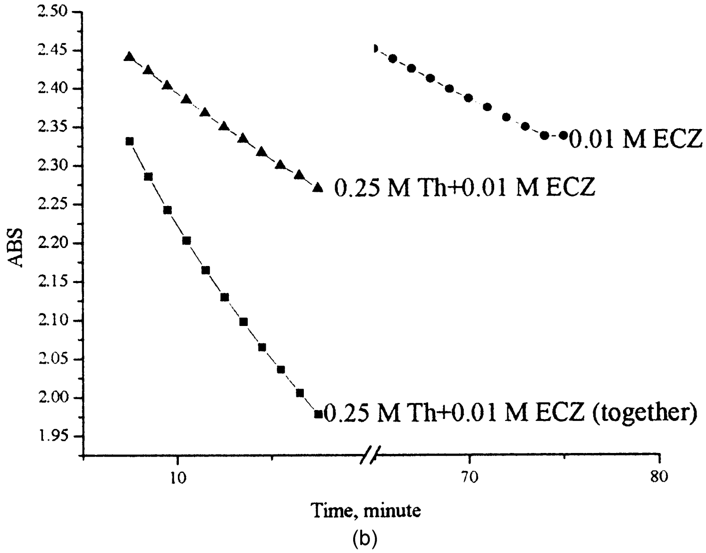


**FIGURE 10b** Variation of peak absorbance (at $\lambda = 811$ nm) values of the solution obtained by 90 seconds oxidation of 0.01 M ECz (●) and after the addition of 0.25 M Th (▲) and the solution obtain by 90 seconds oxidation of 0.25 M Th and 0.01 M ECz (■).

rapidly in 10 minutes. (Figure 10b, curve ▲). On the other hand, when the two monomers were oxidized together the decrease in the absorbance values was the fastest of these three cases (Figure 10b, curve ■). Reaction rates calculated from the slopes of curves in Figure 10b were $1.4 \times 10^{-2}$, $1.8 \times 10^{-2}$, $4.6 \times 10^{-2}$ for 0.01 M ECz, 0.01 M ECz + 0.25 M Th (addition of Th after electrolysis of ECz), 0.01 M ECz + 0.25 M Th (electrolysis together), respectively. These results suggest that cation radicals of ECz react with both Th monomer and its cation radicals, resulting in copolymers in solution. Comparison of reaction rates calculated from Figure 10a and Figure 10b suggests that initiation rate through ECz radical cations is higher than that of Th. This seems reasonable, since the oxidation potential of ECz is lower than Th and oxidation at same potential will give more concentrated ECz radical cations, resulting in higher rates.

## CONCLUSIONS

Results obtained in this study suggest that Th cation radicals react with ECz both in solution and at electrode surfaces. On electrode surfaces, although the percentage of incorporated ECz was low, the polymerization of Th became more facile due to the incorporation of ECz. Ex-situ measurements support the idea that polymerization goes through the reaction of monomers both with their cation radicals and with the cation radicals of the other monomer. The new polymer has the properties of both starting monomers. On the other hand, in-situ measurements allow the determination of soluble intermediates and to match their maximum absorbances with their corresponding CV peaks. Cooligomeric species of Th-ECZ (which give peaks at 376, 400 nm) are consistent with the findings from CV measurements (current).

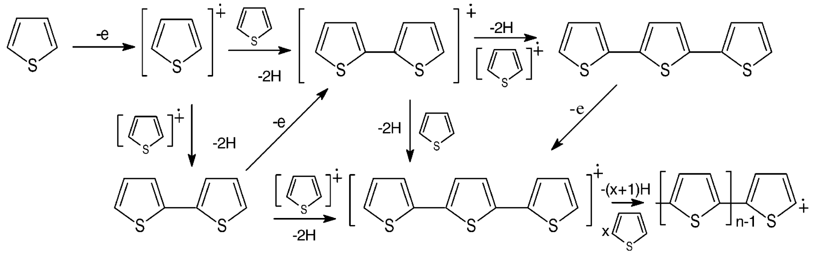
CV's of PECz, PTh and P[Th-co-ECz] formation indicate shifts in $E_p$ and corresponding current changes. Increase in peak currents intensities of ECz in the presence of Th, and solid-state conductivities of copolymer and current values of electrocopolymer growth are indicative of copolymerization. These combined methods give an ability to control the electrocopolymerization growth on both Pt and ITO and consequently in solution and helping to understand the interaction of co-oligomeric species in solution, which will help in obtaining industrially feasible conjugated copolymer structures. This could also be informative for the proper comonomer synthesis, which we are now planning to do.

A tentative mechanism is given in Scheme 1, in the light of our results and the proposed mechanism for the polymerization of Th [4].

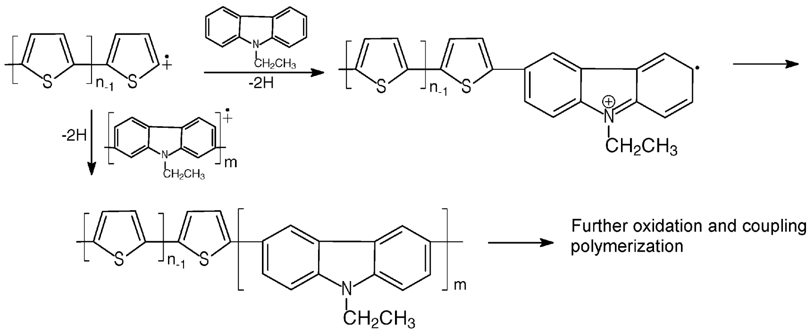
The same mechanism can be written for ECz (depending on real oxidation potential of monomer in such medium) (see Scheme 2). The peaks observed during in-situ measurements seem to correspond to these intermediates.

ECz can be replaced instead of Th and similar species can be initiated from radical cation of ECz.

When simple Woodward-Fieser rules for the calculation of absorption maxima of diens and polyenes [41, 42] are applied to our situation,



**SCHEME 1**



**SCHEME 2**

the observed maxima suggest such intermediates as shown above. However, further calculations are needed for an exact match.

The oxidation of Th is irreversible. This result shows that the Th radical cation formed in the first step is extremely reactive and readily couples and forms its dimer. As for the occurrence of a peak at 320 nm, which corresponds to bithiophene in the UV-Visible spectrum of Th, it suggests that n is most probably 2 or higher numbers. For soluble oligomers it might not be higher than 5. Similar conclusion can be drawn from the experimental result of ECz. Two absorption bands, one near 811 nm and around 390 nm in agreement with literature finding [33] for (oxidized) 3,3′-dicarbazyl, suggest a number of 2 or higher for m. On the other hand, the basic component of the polycarbazole network was suggested to be a tetramer [33]. Therefore, the copolymer film on electrode surface probably has tetramer and higher oligomers of ECz in the polymer chain.

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