Electrocopolymerization of Indole and Thiophene: Conductivity-Peak Current Relationship and In Situ Spectroelectrochemical Investigation of Soluble Co-Oligomers

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Electropolymerization of indole (IN) in the presence of thiophene (Th) was followed by in situ and ex situ spectroelectrochemical studies. A correlation between absorbance (390 nm) and charge (at 600 mV) values indicated that oligomeric species were formed in solution, and similar results were found with in situ measurements. The increase in conductivity by the incorporation of Th into polyindole was about 60 times for a feed ratio $n_{IN}/n_{Th} = 1:10$ and 19 times for $n_{IN}/n_{Th} = 1:1$. Similar effects were also observed during in situ spectroelectrochemical measurements of copolymer formation. It was also found that the cyclic voltametry peak potentials for the electrogrowth of copolymer films were closely correlated to the conductivities of the corresponding films (measured separately by four-point probe method), thereby allowing us to use the peak potential currents to predict the final copolymer film conductivities during the electrochemical growth process. The T_g value of the polymer also increased with the incorporation of Th. The results strongly suggest that IN and Th copolymerize on the electrode surface as well as in solution.

Keywords: Conductivity; Cyclic voltametry; Electrochemical poly-
merization; Indole-thiophene copolymer; Spectrophotometric
measurements

INTRODUCTION

The electrochemical polymerization of indole (IN) was first described
by Garnier and coworkers[1–2]. Further attention has been paid recently
to the polymerization of indole and its derivatives[3–16]. In these studies
the determination of the monomer coupling site, the structure of the
polymer chain, and the electro-oxidation mechanism of indole have been
investigated both experimentally and theoretically. The extent of elec-
trochemical polymerization of IN, initiated by the formation of unstable
IN radical cations at the vicinity of anode and anode surface, depends on
the substituents on IN (due to steric effect). Polyindole film was soluble in
acetonitrile (ACN) to a certain extent, which has permitted spectroscopic
investigation of polyindole formation in solution through oligomeric
stages by in situ spectroelectrochemical measurements[6,10,13,16].

Among conducting polymers, the thiophene-based polymers and oligo-
mers have received the most attention because of their unique electrical
properties and their environmental stability necessary for a number of
practical applications[17–22]. For example, these materials have been used
in electron-beam lithography and as active semiconducting materials in
organic thin film transistors. Soluble thiophene (Th) oligomers contain-
ing 3–12 thiophene units (or other analogous comonomer units) result in
decreased oxidation potentials. The polymeric structure may be idealized
as regularly α-linked polymer chains. However, the synthesis of these
polymers is time consuming and tedious[17–22].

The key to obtaining electrically conductive and redox-active random
copolymers by electropolymerization of heterocyclic monomers is the
oxidation potentials of the corresponding monomers. During the oxi-
dation of a monomer, a polymer may also be deposited on the electrode
surface. In the case of a monomer such as thiophene, which has a higher
oxidation potential relative to its polymer, the high potential applied to it
may cause some degradation of the resulting polymer. This problem can
be overcome by changing the comonomer structure, e.g., extending the
conjugation of the monomer and using monomers that result in signif-
icant reduction in the oxidation potentials.

The high oxidation potential of Th ($\sim$1470 mV versus Ag/AgCl)
compared to its polymer (PTh) causes some degradation of the polymeric
film. Introducing IN moieties into the polymer structure will result in a
decrease in the oxidation potential. Therefore, investigation of indole

polymerization in the presence of Th will be helpful to clarify the reaction pathway of the incorporation of Th into the copolymer structure as well as the improvement of the properties of polyindole (PIN), especially thermal and electrical conductivity.

EXPERIMENTAL

IN and Th were acquired from Fluka and used without further puri-fication. A Wenking POS model 73 scanning potentiostat connected with Kipp and Zonen X-Y Recorder and interfaced to a PC was employed for electrochemical measurements. Constant potential electrolysis was per-formed using HPLC-grade acetonitrile (ACN) containing 0.1 M NaClO$_4$ as the electrolyte, Pt as a working electrolyte, Ag/AgCl–covered Ag wire as a reference electrode, and Pt as a counter electrode. A Shimadzu 160A UV-Visible spectrophotometer was used both for in situ and ex situ spectroelectrochemical studies. Fourier transform infrared (FT-IR) measurements were performed on a Mattson 1000 FT-IR spectrometer. Conductance measurements were performed on freestanding polymeric films removed from electrode surfaces with a Keithley 617 electrometer connected to a four-point probe head with gold tips.

RESULTS AND DISCUSSION

Spectroelectrochemical measurements were performed at a potential up to 1200 mV in order to allow oxidation only of IN. (Oxidation of Th is about ∼1470 mV versus Ag/AgCl.) This maximum potential permitted the measurements of copolymers containing neutral Th.

The oxidation potentials of the monomers IN and Th ($E_{pa} = 1470$ mV and $E_{pa} = 1100$ mV, respectively) were different. From polarization curves of IN and Th, a proper ratio was determined that optimized the copolymerization under the given reaction conditions. Oxidation of IN at the Pt electrode took place at about 740 mV, and upon multiple cycling two new peaks at about 300 and 600 mV versus Ag/AgCl were observed; see Figure 1(a). Peak intensities increased with cycling, suggesting the formation of PIN on the electrode surface. In the presence of Th at mol ratio of $n_{IN}/n_{Th} = 1:1$, the cyclic voltammetry (CV) of IN monomer became different from the CV of IN alone; see Figure 1(b). The second anodic peak (600 mV) shifted to a lower potential (570 mV), and the first peak (at 300 mV) was observed as a shoulder. In the reverse direction, two peaks were found, in contrast to the result of IN alone. In order to enhance copolymerization kinetically, the Th concentration was increased 25 times, and the CV of this mixture ($n_{IN}/n_{Th} = 1:25$) was different from the CV of IN alone and the CV of the previous IN + Th mixture ($n_{IN}/n_{Th} = 1:1$); see Figure 1(c).
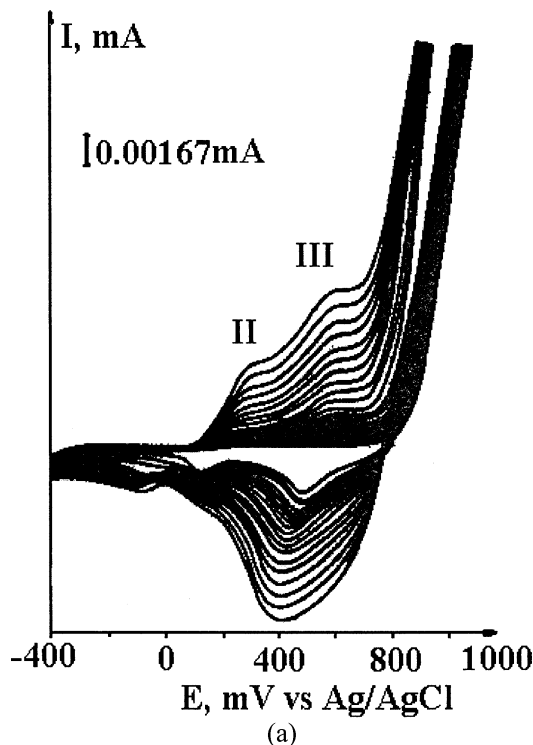
FIGURE 1 Cyclic voltamograms of 0.01 M IN (a) IN + Th mixture ($n_{IN}/n_{Th}=1:1$) (b) ($n_{IN}/n_{Th}=1:25$) (c) in 0.1 M NaClO$_4$ containing acetonitrile solution obtained during in situ spectroelectrochemical measurements. Scan rate $= 100\,mV\,s^{-1}$.

The results may be rationalized via the formation of radical cations during electropolymerization. The IN radical cation may encounter another monomer or oligomer radical and couple with it. Alternatively, the radical cation may react with a neutral Th monomer molecule (and two α-hydrogens are then split off as protons), causing a shift in E_p depending on the content of IN and Th. (Note that for the copolymer with $n_{IN}/n_{Th}=1:1$, $E_{p2}=570\,mV$; for copolymer with $n_{IN}/n_{Th}=1:25$, $E_{p2}=750\,mV$; for PIN, $E_{p2}\sim600\,mV$); see Figures 1(b), 1(c), and 1(a), respectively. Incorporation of Th into the copolymer structure shifts E_{p2} to a more positive potential (from $\sim600\,mV$ to $750\,mV$), and the polymeric film formation can be followed by an increase in the current densities upon repetitive cycling. The currents are about tenfold higher when Th is in excess ($n_{IN}/n_{Th}=1:25$), Figure 1(c), than the currents of corresponding peaks in Figures 1(a) and 1(b).

FIGURE 1 (*Continued.*)
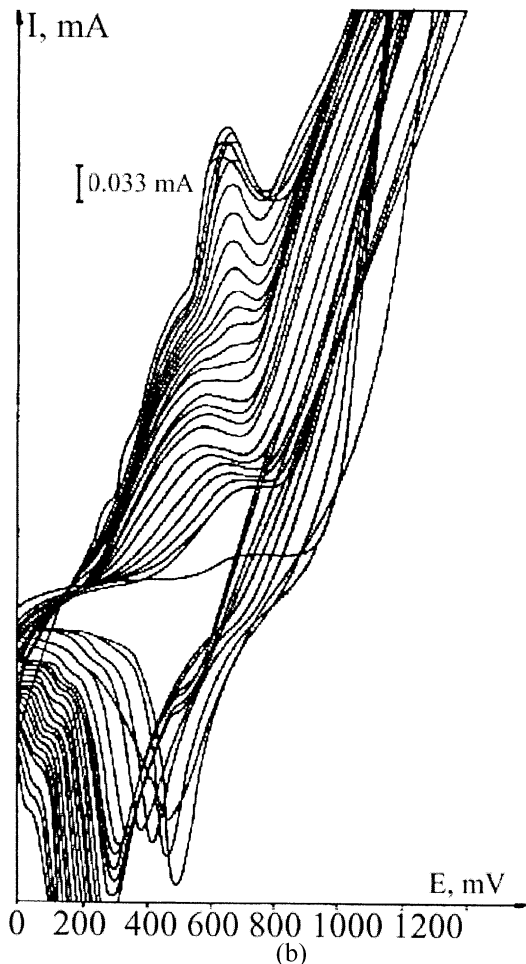
The heights of anodic peak currents at potentials around 450 and 750 mV, $n_{IN}/n_{Th} = 1{:}25$, Figure 1(c), can be compared to the copolymer with $n_{IN}/n_{Th} = 1{:}1$ at $E_{p2} = 570$ mV, Figure 1(b), the homopolymer PIN, Figure 1(a), at $E_{p1} = 300$ mV and $E_{p2} \sim 600$ mV (monomer oxidation at $E_{pa} = 1100$ mV), and the homopolymer PTh (monomer oxidation at $E_{pa} = 1470$ mV). The E_{p2} current values are 2.40 mA, 0.36 mA, and 0.008 mA for $n_{IN}/n_{Th} = 1{:}25$, 1:1, and PIN, respectively, which are on the order of about 300/45/1. Thus, the presence of Th in the copolymer gives 300 times higher current if the Th/IN ratio is 25, and 45 times higher
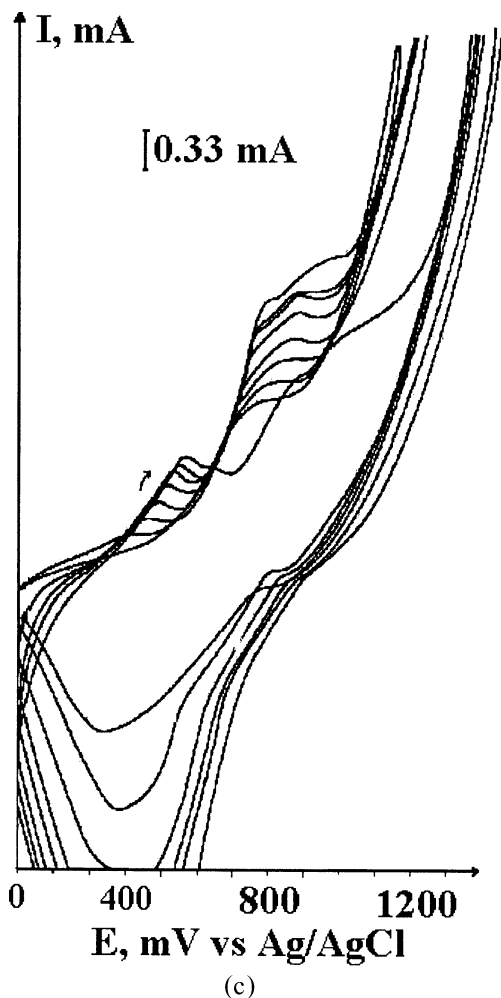
(c)

FIGURE 1 (*Continued.*)

current if the Th/IN ratio is 1. This result indicates that the better con-
jugation of Th increases the conductivity of indole in the copolymer. One
may suggest that without estimating the (co)polymer surface coverage
(e.g., relative thicknesses), the larger currents observed cannot be used to
infer that one polymer is more conducting than another, and the currents
may reflect many things such as the polymerization rate. However, the
above findings are also corroborated by the solid state conductivity of the
resulting copolymers (Table II and Figure 8). Since the conductivity of

the PTh film (measured by the four-point probe) is much higher than the conductivity of the PIN, the fact that an increase in Th feed ratio results in a conductivity increase indicates the formation of new polymer film from Th and IN. In view of the electropolymerization current values, this solid state conductivity result can be reliably interpreted only if the film thickness is the same in all cases (8.0, 8.5, 9.0 μm for PIN, and copolymers with n_{IN}/n_{Th} ratios of 1:1 and 1:25, respectively).

Scan rate dependence was determined for PIN and the copolymers. As illustrated by Figure 2 for PIN, the current is proportional to the scan rate, indicating that all electroactive sites are electrode supported. Formal potentials ($E_{1/2}$) of the PIN and copolymer films were determined from these measurements and found to be 0.20 V, 0.25 V, and 0.29 V for PIN and copolymers at $n_{IN}/n_{Th} = 1$ and 25 mol ratios, respectively. The shift in potential again confirms the occurrence of copolymer formation.
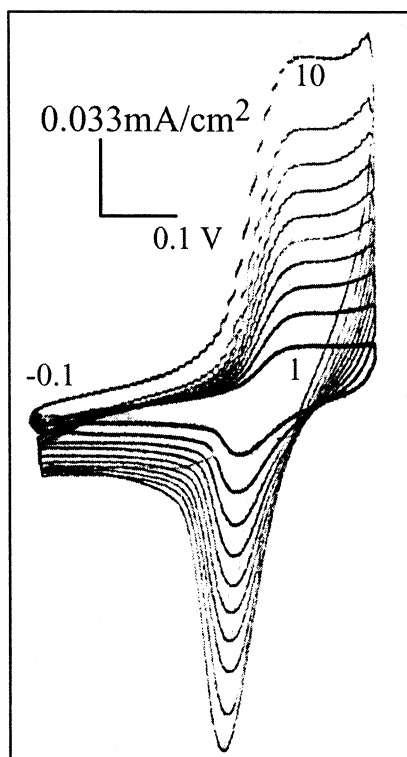
FIGURE 2 Current and scan rate dependence of polyindole (PIN).

UV-visible spectra of IN and IN + Th mixture ($n_{Th}/n_{IN} = 1$) were obtained during the in situ spectrophotometric measurements; see Figures 3(a) and 3(b). IN shows three peak maxima, which increase with time; see Figure 3(a). In the presence of Th additional maxima occurred and their absorbances increase more rapidly than those of IN alone; see Figure 3(b).

The variation of these absorbances with time is given in Figures 4(a) and 4(b). In the presence of Th the absorbance values increased more rapidly than indole, suggesting that a reaction between Th and IN had occurred; see Figure 4(a). In the case of IN, the maximum absorbance values at 390 nm and the charge values at $E_{pa} = 630$ mV show a similar trend with time, suggesting that both correspond to the same species; see Figure 4(b). A one-to-one correspondence between absorbance (at 390 nm) and charge (at about 600 mV) is observed for oligomeric species that are formed during in situ spectroelectrochemical measurements. When Th was oxidized, a blue-colored solution was formed that had a maximum at 659 nm (Figure 5, curve a). The addition of IN monomer into this solution decreased the absorbance quickly and shifted the wavelength (Figure 5, curve b). A new maximum absorbance at 325 nm occurred, and its absorbance value increased with time (Figure 5, curve c). In our previous work, two peaks were observed at 347 and 390 nm during the in situ spectroelectrochemical polymerization of IN[16]. Being different from the maximum absorbances of Th and IN alone, these peaks confirmed the formation of soluble oligomers from Th and IN, indicating that oligomeric Th species can react with neutral IN molecules or vice versa.

In the FT-IR spectra of the copolymer it is possible to observe characteristic bands of both Th and IN (Figure 6). The most characteristic difference in the copolymer is the decrease in the intensity of the band at 1340 cm^{-1}, which is characteristic of oxidized polythiophene[23,24]. The band at 1100 cm^{-1}, due to the incorporation of ClO_4^- ions[10], appeared in both PTh and the copolymer; see Figures 6(a) and 6(b). The band at 1540 cm^{-1} due to the bending mode of the N–H bond was observed in Figures 6(a) and 6(c). Another noticeable feature in the spectrum is the absorption band around 790 cm^{-1}, which indicated polymerization through the α-position of each monomer and supported the idea of formation of the copolymer of IN and Th.

The differential scanning calorimetry (DSC) curves of Th and IN showed the glass transition temperature, T_g, around 120°C and 65°C, respectively (Table I). In the case of copolymers, an increase in Th resulted in an increase in the T_g value, as expected. The observation of only one T_g value suggested the formation of a random copolymer rather than a block copolymer.

The formation and growth of the polymer films on platinum electrodes from solution was followed by gravimetric determination of the polymer grafted on the electrode as suggested in the literature[10]. The reaction rate
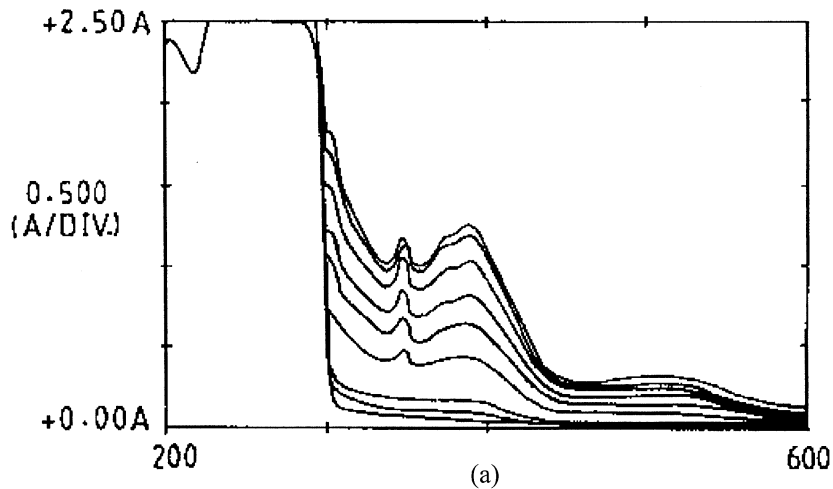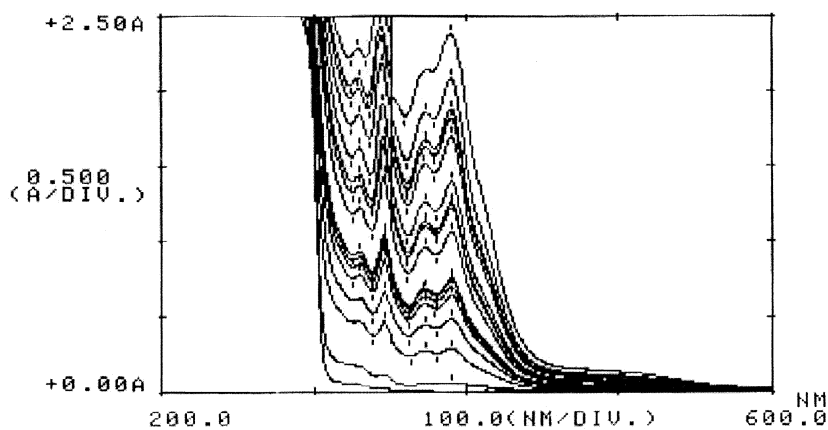
FIGURE 3 UV-visible spectra of IN (a) and Th + IN mixture ($n_{IN}/n_{Th} = 1{:}1$) (b) obtained during in situ spectroelectrochemical measurements ([NaClO$_4$] = 0.1 M, [IN] = 0.1 M, $n_{IN}/n_{Th} = 1{:}1$, potential = 1.2 V in ACN.)

was found inversely proportional to IN concentration and proportional to Th concentration. In order to interpret the data, more studies are needed.
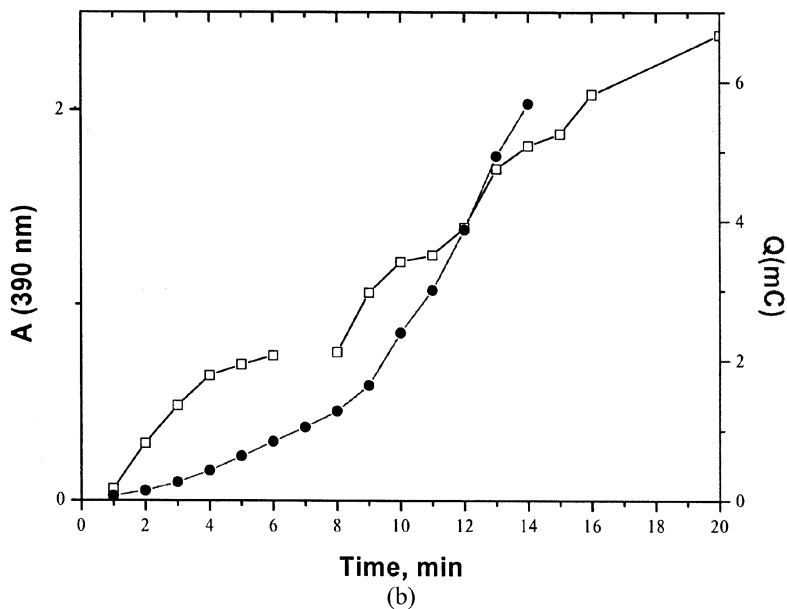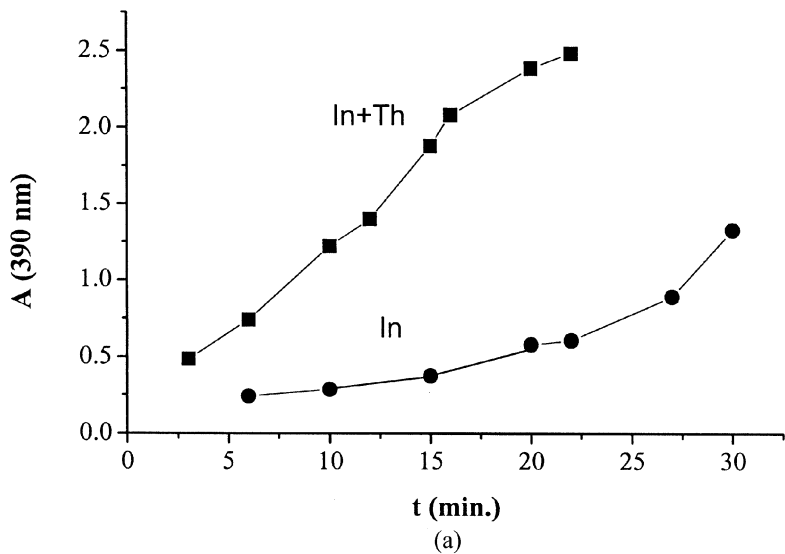
FIGURE 4 Variation of peak values with time obtained during in situ spectro-electrochemical measurements of IN and IN + Th (n_{IN}/n_{Th} = 1:1) (a) and variation of absorbance (λ = 390 nm) and charge values (for peak at 630 mV) with time obtained during in situ spectroelectrochemical measurements (b). ([NaClO$_4$] = 0.1M, [IN] = 0.1 M, n_{IN}/n_{Th} = 1:1, potential = 1.2 V in ACN.)
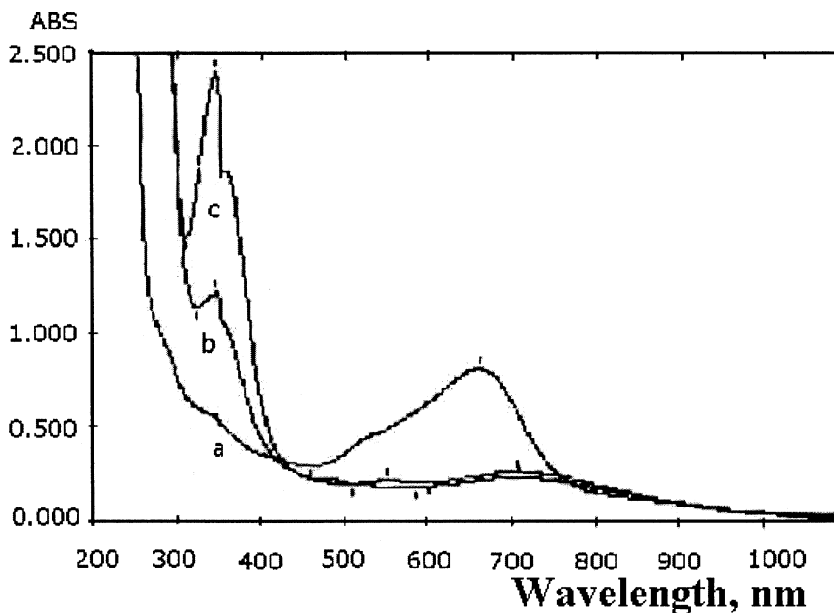
FIGURE 5 UV-visible spectra of 0.25 M Th after 90 s electrolysis (a) and addition of 8.6×10^{-3} M IN immediately (b) and after 2 min (c). ($[NaClO_4] = 0.1$ M, potential $= 1.7$ V in ACN.)

The conductivity of IN is very low, about 10^{-5}–10^{-7} Scm^{-1} as reported in the literature[6,10]. Although the incorporation of Th is not high due to kinetic reasons, the conductivity increase by incorporation of Th into the copolymer structure (Table II) indicates copolymerization of IN and Th (with low content of Th). Since IN is more easily oxidized than Th, these findings suggest that IN is transformed to oligomers through radical cation coupling, followed by copolymerization with oxidized Th oligomers. An alternative scenario is the reaction of IN oligomeric radical cations with neutral Th molecules.

While PIN is soluble in ACN, PTh is not. Thus, the solubility of the reaction product between IN and Th at different ratios was investigated. The results were plotted together with the maximum absorbance values at $\lambda = 390$ nm that correspond to IN (Figure 7). As the level of Th increases in the copolymer, the solubility in ACN decreases. This result is consistent with copolymer formation between IN and Th.

There was an interesting trend between the current (mA) of E_{p2} of copolymer electrogrowth on Pt versus the initial IN content of
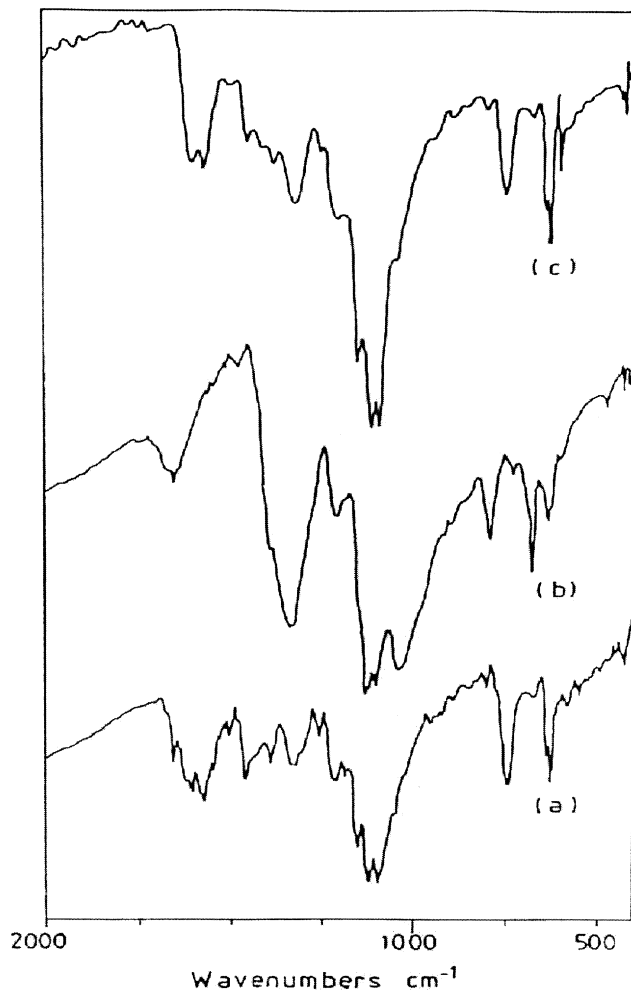
FIGURE 6 FT-IR spectra of PIN (a), PTh (b), and copolymer (c). ([NaClO₄] = 0.1 M, [IN] = 0.1 M, n_{IN}/n_{Th} = 1:1, potential = 1.2 V in ACN.)

copolymer ($n_{IN}/(n_{IN} + n_{Th})$ (mole fraction of IN in the feed) and the conductivity (mS/cm) (obtained by four-point probe method) of the resulting copolymer versus [$n_{IN}/(n_{IN} + n_{Th})$] (Figure 8). This indicates that the currents of the CV peak potential of electrogrowth of copolymer films are closely correlated to the conductivities of the corresponding films, allowing us to use the current of peak potentials for the prediction
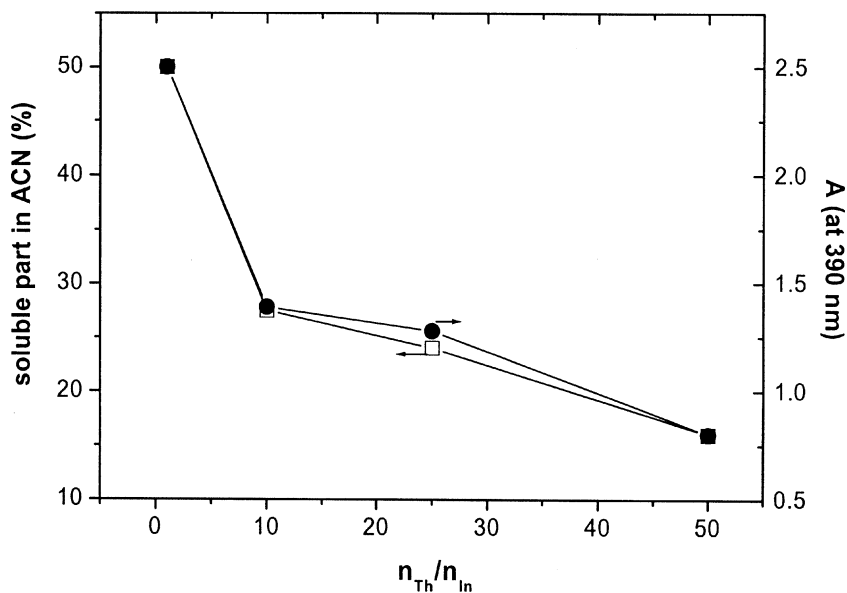
TABLE I Glass transition (T_g) temperatures of polymers

Polymer	T_g,°C
PTh	120
P[IN-co-Th] ($n_{Th}/n_{IN} = 25$)	95
P[IN-co-Th] ($n_{Th}/n_{IN} = 1$)	90
PIN	65

TABLE II Conductivities of polymers and copolymers (measured by the four-point probe method)

Polymer	Conductivity, mS/cm
PTh	42.00
P[IN-co-Th] ($n_{IN}/n_{Th} = 1:10$)	1.80
P[IN-co-Th] ($n_{IN}/n_{Th} = 1:1$)	0.56
PIN	0.03

[IN] $= 0.01$ M, [NaClO$_4$] $= 0.1$ M (at 1.3 V).

FIGURE 7 Variation of solubility and maximum absorbance values at $\lambda = 390$ nm that corresponds to IN with n_{IN}/n_{Th} ratio.
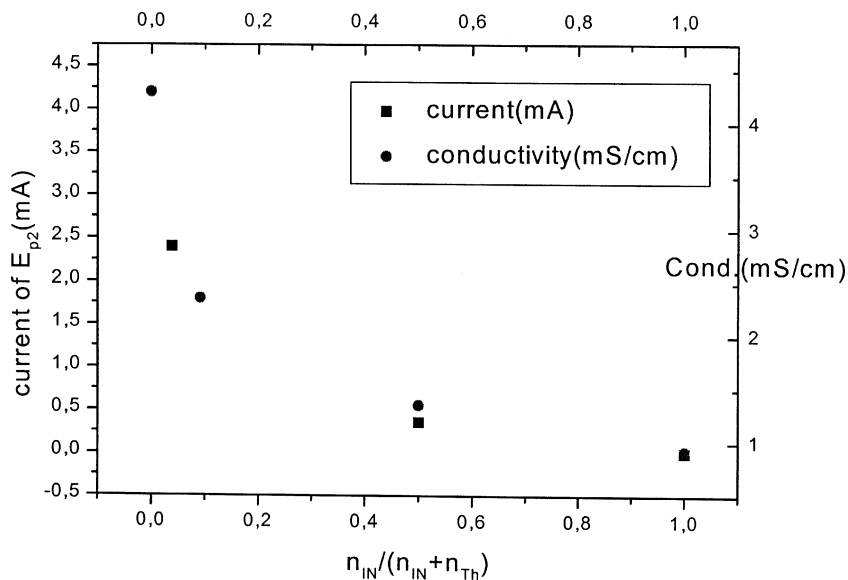
FIGURE 8 Current(mA) of E_{p2} of copolymer electrogrowth on Pt versus initial IN content of copolymer $[n_{IN}/(n_{IN} + n_{Th})]$ (fraction of IN) and conductivity (mS/cm) (by four-point probe) of resulting copolymer versus its fraction of IN content in initial copolymer feed $[n_{IN}/(n_{IN} + n_{Th})]$.

of final copolymer film conductivities during the electrochemical growth process.

CONCLUSION

In our studies of electroactive copolymers having improved physical properties, we found the correlation between absorbance and charge for electroactive oligomeric species obtained from in situ spectrophotometric and conductivity measurements of the copolymers to be a good tool for the determination of these species.

It was also found that the CV peak potentials of the electrogrowth of copolymer films are closely correlated to the conductivities of the corresponding films, which are measured separately by the four-point probe method, allowing us to use the current of peak potentials for the prediction of final copolymeric film conductivities during the electrochemical growth process.

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