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# *Electrochemical polymerization of thionaphthene–indole*

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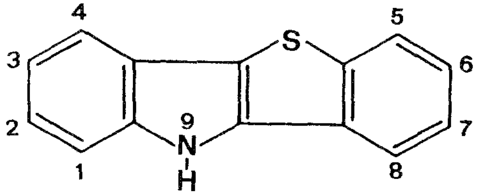
The polymer deriving from thionaphthene–indole has been prepared by electrochemical oxidation of the monomer in methylene chloride on platinum electrode. The oxidized polymer so obtained has been reduced on the same electrode to a neutral polymer, which is processable and soluble in several solvents. Both oxidized and neutral polymers have been characterized by UV, IR and mass spectrometry. The electrical conductivity of the oxidized material has been found to be nine orders of magnitude greater than that of the reduced product.

## 1. Introduction

In recent literature a growing number of papers have been concerned with the electrochemical synthesis of polymers with special electrical properties (conductivity and photoconductivity) [1–7].

In this paper we deal with the electrochemical polymerization of thionaphthene–indole (TNI).



TNI is an heterocyclic molecule with two different heteroatoms (N and S), which shows a strong charge photogenerating power [8]. For this reason the polymerization of TNI could lead to photoconducting material suitable for energy photoconversion studies.

In previous work [9] the polymerization of *N*-allyl-thionaphtheneindole (ANTI) has been described and the stability of the corresponding polymer, obtained as an oxidized molecule, has been pointed out. In the present work, besides an analogous electrochemical synthesis of the oxidized polymer of TNI, the electrochemical reduction of this polymer to a neutral molecule has been carried out. The electrical conductivity of both of the oxidized and neutral polymer has been measured.

## 2. Experimental details

Thionaphthene–indole was supplied by Ferrania S.p.A. and purified by chromatography, sublimation and zone refining in consecutive steps. Methylene chloride (Merck pro analysis and Aldrich Gold Label) was distilled over $P_2O_5$ in a nitrogen atmosphere. Tetrabutylammonium perchlorate (TBAP) (Fluka purum) was crystallized from methanol, lithium perchlorate (Fluka purum p.a.) was used as supplied. Tetrahydrofuran (THF) was an Uvasol Merck product.

Diffusion layer renewal voltammetry, cyclic voltammetry and electrolyses of TNI were performed in 0.1 M TBAP methylene chloride solutions using a multifunction AMEL Electrochemolab instrument. The reference was a saturated calomel electrode (SCE), to which all potentials are referred in this paper. The platinum counter electrode was separated from the working electrode compartment by a glass

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sintered disc. The working electrode was a platinum micro-electrode for voltammetry and a platinum 1 cm$^2$ plate for electrolysis.

The oxidized polymer, obtained as a black film on the platinum plate by electrolysis of TNI in methylene chloride, was reduced on the same electrode to neutral (yellow) polymer in 0.2 M $LiClO_4$ aqueous solution at $-0.2$ V. The neutral polymer was dissolved in methylene chloride for spectrophotometric purposes or in THF (about 20% in weight) for conductivity measurements. From THF a good quality film was cast on an aluminium semitransparent electrode, prepared on an optical Suprasil plate. The film obtained was heat-cured to remove any trace of solvent and the sandwich completed by depositing a second aluminium layer. The film thickness was determined: (i) from the optical absorption spectrum (ii) with a Talystep.

The conductivity of the oxidized polymer was measured by means of a Keithley 195A digital multimeter on pressed pellets, 0.5 cm in diameter, sandwiched between two platinum conducting electrodes. These samples were about 0.5 cm thick.

The UV–visible spectral analyses were performed with a model Lambda 5 Perkin Elmer instrument. For these measurements the oxidized polymer was prepared as a thin film on an UV Suprasil quartz electrode coated by a conducting semitransparent layer of $SnO_2$.

IR spectrophotometric measurements were carried out of KBr pellets with a model DS701G Jasco grating spectrophotometer. The mass spectra were performed using a double focusing mass spectrometer VG ZAB 2F operating in the electron impact mode (70 eV, 200 A) with source temperature at 200° C.

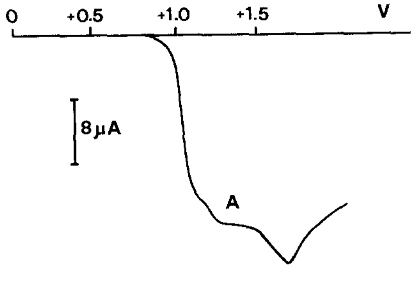

Fig. 1. Diffusion layer renewal voltammetry on a platinum electrode of $1.36 \times 10^{-3}$ M TNI in methylene chloride (supporting electrolyte, 0.1 M TBAP).

All electrochemical experiments were carried out at room temperature (~22° C). While the voltammetry was run on deaerated samples, the electrolysis was performed without deaeration, because oxygen did not affect these experiments significantly.

## 3. Results and discussion

### 3.1. *Electrochemical measurements and preparation of the polymer*

The diffusion layer renewal voltammetry of TNI (Fig. 1) shows an anodic wave A with $E_{1/2} = +1.04$ V. At low concentrations, i.e. [TNI] $\cong 1 \times 10^{-3}$ M, electrolyses at potentials corresponding to the plateau of this wave (1.2 V) lead to soluble products, with a consumption of about 1.5 electrons per molecule of monomer. At higher concentrations ($\cong 2 \times 10^{-3}$ 10 M) this value increased and approaches 2 and, at the end of electrolysis, a very thin black solid layer is observed on the electrode. In the same diffusion layer renewal voltammetry an increase of current is observed from + 1.4 to 1.5 V. Though the faradic process operative at these potentials has not been determined, it is to be pointed out that oxidation potentials of thio-heteroaromatics are in the range + 1.6–1.8 V [10].

The diffusion layer renewal voltammetry of TNI is very similar to that of ATNI. By oxidizing ATNI at + 1.8 V, passivation of the electrode was observed; only at + 2.5–3 V did polymer film deposit on the electrode but, at these potentials, the alkyl double bonds can also be involved in the electrode reaction, leading to a cross-linked polymer [9]. In the case of TNI, which does not have unsaturated side chains, the polymer must be formed, in the same experimental conditions, by a coupling reaction of radical cations localized in the aromatic moiety. As for ATNI, electrolysis of TNI at + 1.8 V leads to electrode passivation after the flow of a very small amount of charge.

The cyclic voltammetries of TNI from $-1$ to $+1.3$ V and $+2$ V are respectively shown in Fig. 2a and Fig. 2b. In particular, the cyclic voltammetry until $+1.3$ V presents two main peaks ($\alpha$ and $\beta$), the electrochemical interpretation of which is still not fully defined [11]. In the

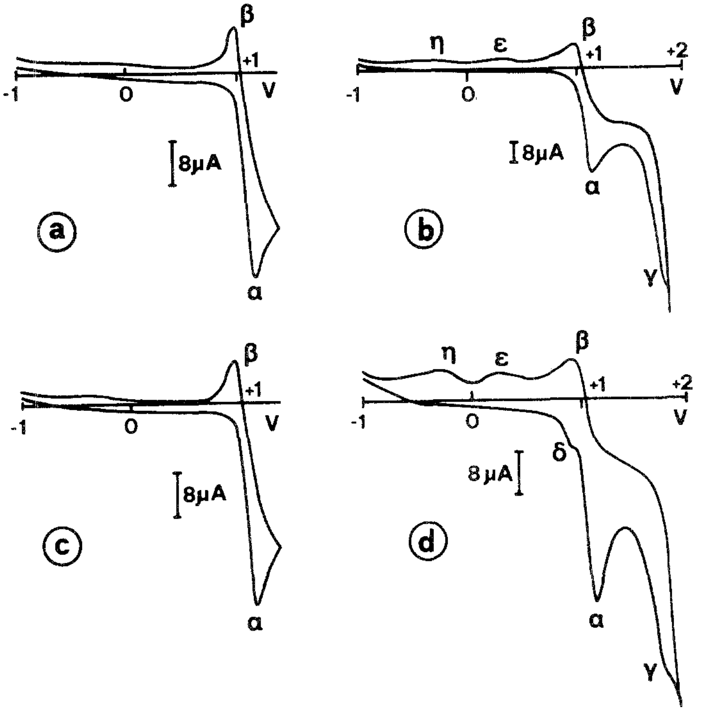

Fig. 2. Cyclic voltammetry of $1.04 \times 10^{-3}$ M TNI in methylene chloride on a platinum electrode (supporting electrolyte, 0.1 M TBAP): (a) from − 1 to + 1.3 V (first cycle); (b) from − 1 to + 2.0 V (first cycle); (c) from − 1 to + 1.3 V (12th cycle); (d) from − 1 to + 2.0 V (12th cycle).

cyclic voltammetry of Fig. 2b, which reaches higher potentials, the anodic current increases after the first oxidation peak, $\alpha$, showing a small flexus, $\gamma$, at + 1.7 V where, however, the voltammetry is not yet reliable owing to solvent discharge. After the second cycle, while the peaks $\alpha$, $\beta$ and $\gamma$ decrease, the peak $\delta$ appears, which increases in the subsequent cycles (Fig. 2d); this peak is missing in repetitive cyclic voltammetry until + 1.3 V (Fig. 2c). This voltammetric behaviour of TNI agrees with the growth, at potentials anodic of + 1.3 V, of a film the oxidation of which should be associated with the peak $\delta$, while its reduction peak could be $\varepsilon$ at + 0.3 V or $\eta$ at − 0.3 V. Also the passivation of the electrode, shown in diffusion layer renewal voltammetry at potentials anodic of + 1.5–1.6 V, suggests the formation on the electrode of a film which is not highly conductive.

To overcome the passivation and synthesize the polymer, the electrolysis potential was increased to more anodic values (+ 2.5–3 V), where the solvent itself can be oxidized [12]. Although this process cannot be excluded, it is to be noted that, due to the electrode passivation, the solvent discharge should also occur at more positive potentials than on clean platinum electrode (~ + 1.9 V). Indeed, during the electrolysis at + 2.5–3 V, after the flow of some coulombs, a black solid begins to deposit on the electrode, but its adhesion, which depends on current density, is not very high and the product comes off the electrode, falling to the cell bottom as a black powder. The electrolysed solution becomes red-brown, owing to the formation of soluble products, probably dimers, as observed in other cases [5, 13]. The polymerization does not occur at the potential of the first wave A, where the oxidation should involve a nitrogen-centred orbital, as can be inferred from the $\pi$ electron cloud density in similar molecules [14, 15]. At this potential, only soluble red-brown products are formed by electrolysis. The polymerization occurs at potentials anodic of + 1.3 V where, owing to a different oxidation path (formation of the monomer dication as hypothesized for 2,2′-thienylpyrrole [16]?), a subsequent coupling reaction can concern a greater number of positions in the TNI molecule. The overall mechanism of the polymerization process is

$$nMH_9 - xn(e) \longrightarrow [MH_{(9-y)}]_n^{n(x-y)+} + ynH^+ \qquad (1)$$

where $MH_9$ represents TNI.

The elemental analysis of the oxidized polymer (C = 57.17%, H = 5.50%, N = 4.38%, S = 6.33%, Cl = 10.43%, O = 16.10%) agrees with the formula:

$$\{[(C_{14}H_{6.6}NS)^{0.91+}(0.91ClO_4^-)]0.6\ TBAP\}_n \qquad (2)$$

where the weight of the repeat unit is 516.4.

Considering that the formula of TNI is $C_{14}H_9NS$, it may be inferred that the number of bonds between the repeat units is not 2 but 2.4, so revealing the formation of cross-linked material. Moreover, it is to be noted that the inclusion of supporting electrolyte has already been found in the polymer deriving from ATNI in the same conditions [9]. By flowing 100–110 C in the TNI solution, 50–55 mg of polymer are obtained. Taking into consideration formula 2) and the reaction mechanism 1), the charge consumed seems too high with respect to the theoretical value (~30 C), with a current yield of ~30%. However, this can be accepted taking into account the formation of soluble products and the contribution of the solvent reaction at the electrode.

The neutral product, obtained by electrochemical reduction of the oxidized polymer, is very soluble in methylene chloride. Therefore, cycling voltammetric experiments on the polymer (Fig. 3) were run in water, by using an electrode coated by a film of oxidized polymer and $LiClO_4$ as supporting electrolyte. The limits of these experiments are given by the poor quality of the polymer coat (both on a platinum Pt and a $SnO_2$ electrode), the thickness of which could neither be directly measured nor calculated from the amount of coulombs, owing to the simultaneous discharge of the solvent at the working potential. In the cyclic voltammetry of Fig. 3 the irreversibility of the redox processes of the polymer is revealed by the separation between the cathodic peak c and the anodic peaks a and b, which, in reversible systems, must have roughly the same $E_p$. This may be due both to the slowness of counter ion diffusion and to the experimental conditions of preparation of the polymer (monomer concentration, thickness of the film) [17, 18] and of the cyclic voltammetry (temperature, type and concentration of supporting electrolyte) [18, 19]. it is to be noted that the potentials of the peaks c and b ($E_{p(c)} = +0.2$ V, $E_{p(b)} = -0.85$ V at 100 m V s$^{-1}$) corresponds quite well to those observed in the cyclic voltammetry of TNI and attributed to the formation of polymer ($E_{p(\varepsilon)} = +0.25$ V, $E_{p(\delta)} = 0.90$ V); the peak, $\eta$, in the cyclic voltammetry of TNI is probably due to the reduction of $H^+$ produced in the polymerization (reaction 1).

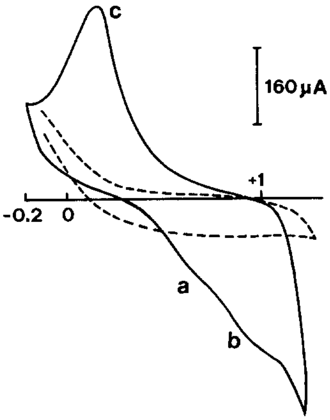

Fig. 3. Cyclic voltammetry of a film of oxidized polymer on a 1 cm$^2$ platinum electrode in 0.2 M $LiClO_4$ aqueous solution (full line). The polymer film was obtained by flowing 18 C through $4.76 \times 10^{-3}$ M TNI in methylene chloride (supporting electrolyte, 0.1 M TBAP). Dotted line: cyclic voltammetry of 0.2 M $LiClO_4$ aqueous solution on a 1 cm$^2$ platinum electrode.

The polymer peaks are broad. Splitting of the anodic peak into two separate peaks, a at +0.65 V and b at +0.85 V, is observed at high sweep rates (100 mV s$^{-1}$), this being slightly evident at low sweep rates (50 and 20 mV s$^{-1}$). Thus the presence of two non-equivalent oxidizable sites in the polymer molecule can be inferred [13, 18]. On the other hand, the singleness of the reduction peak at +0.20 V suggests a charge redistribution following the oxidation reaction.

### 3.2. *Spectrophotometric and mass spectrometric measurements*

The oxidized polymer, peeled off the electrode as a black solid or centrifuged from the solution, was insoluble in most common organic solvents (only slightly soluble in acetone). For this reason

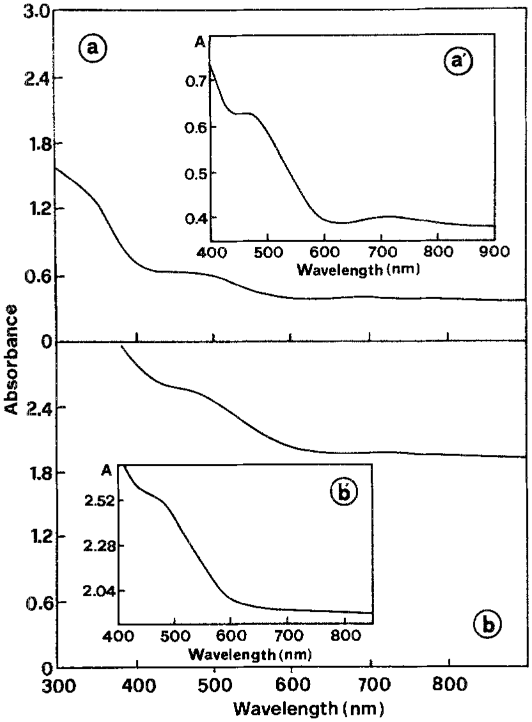

Fig. 4. UV–visible absorption spectra of an oxidized polymer film on a $SnO_2$ electrode, obtained by electrolysis of $5.66 \times 10^{-3}$ M TNI in methylene chloride (supporting electrolyte, 0.1 M TBAP): (a) after the flow of 9.36 C; (b) after the flow of 24 C. (a′) and (b′) are enlarged particulars of (a) and (b).

its spectrum was recorded for solid samples deposited on a $SnO_2$ electrode. This spectrum shows, besides a generalized absorbance in the visible region, a defined band with $\lambda_{max}$ = 470–480 nm and a small broad band centred around 700 nm, which decrease during the electrolysis, while the absorbance all over the visible region increases (Fig. 4a, b). This spectral pattern is similar to that reported in the literature for similar cases [16, 20].

The UV–visible spectrum of the neutral polymer, dissolved in methylene chloride, does not show bands in the visible region, but gives some broad bands in the spectral range of TNI, red-shifted with respect to those of the monomer (Fig. 5a, b).

The IR spectra of TNI and its oxidized and neutral polymers are presented in Fig. 6a–c. Bands in the region 1050–1100 $cm^{-1}$ and at 620 $cm^{-1}$, due to $ClO_4^-$ ions, are observed both for the oxidized and neutral polymer, but their different forms in the two cases reveal different interactions of this ion. The relative amounts of $ClO_4^-$ in the two polymers cannot be quantitatively defined by IR. Nevertheless, the presence of these bands also in the neutral material points out the intimate inclusion of supporting electrolyte in the polymer, as shown by the elemental analysis and by the IR bands at 2800–3000 $cm^{-1}$ and 870 $cm^{-1}$, typical for TBAP. For both polymers the disappearance of the narrow band at 3490 $cm^{-1}$ due to the =NH groups of the monomer is notable. This indicates that position 9 of TNI is one of the preferential points for coupling or other reactions leading to polymerization.

The mass spectrum of the reduced and oxidized is shown in Fig. 7. The very significant peaks at $m/z$ = 222, $m/z$ = 444 and $m/z$ = 663

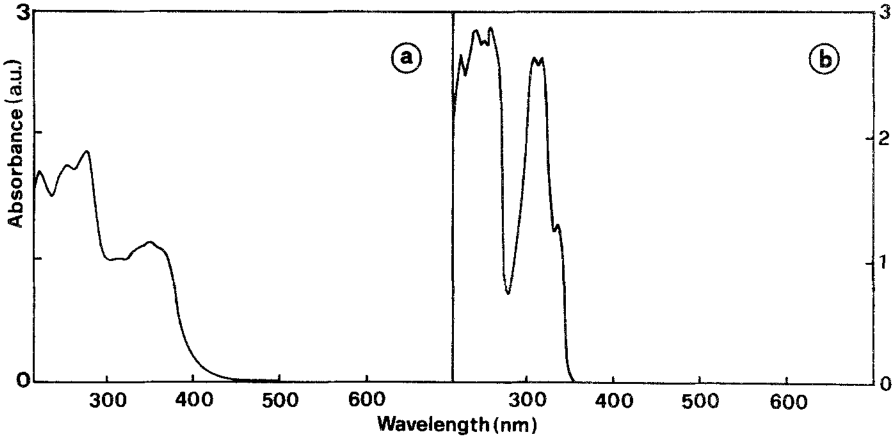

Fig. 5. UV–visible absorption spectra of: (a) neutral polymer in methylene chloride; (b) $1.3 \times 10^{-3}$ M TNI in methylene chloride (optical path, 0.1 cm).

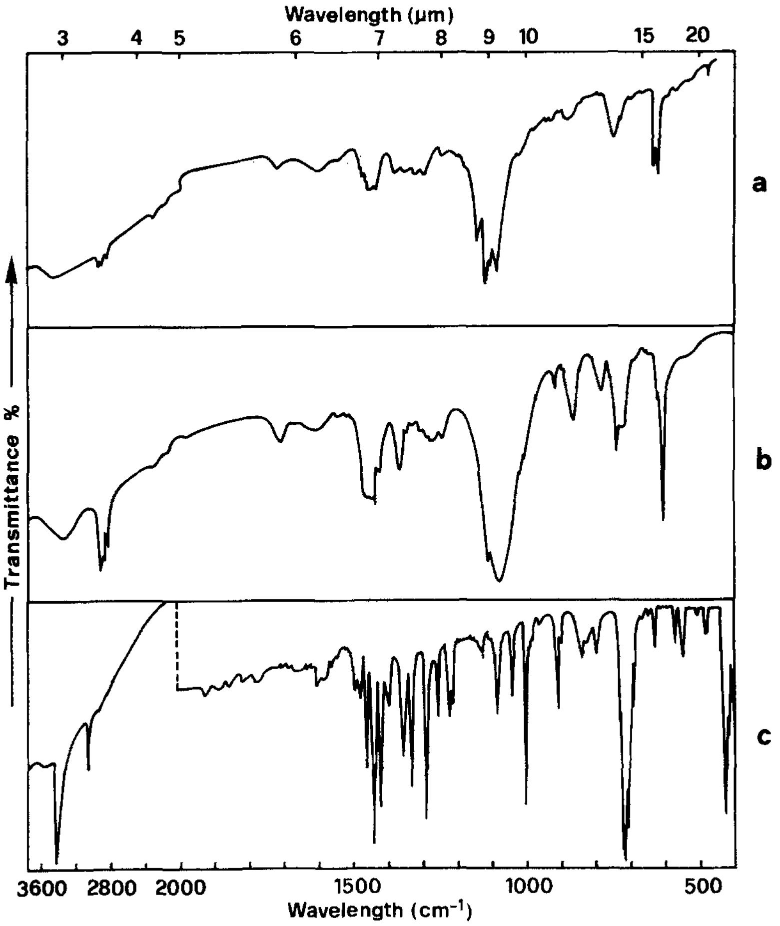

Fig. 6. IR spectra (KBr pellets) of: (a) oxidized polymer; (b) neutral polymer; (c) TNI.

correspond to the deprotonated monomer, dimer and trimer of TNI; the ionic fragments probably relative to the $HS^{\cdot}$($m/z = 411$) and $NH_2^{\cdot}$($m/z = 206$) losses from $m/z = 444$ and $m/z = 222$, respectively, are present.

Numerous and stable double-charged ions are evident; in particular, the ions with $m = 409$, 411, 413, 415, 441, 443, 445, 447 give peaks $m/z = 204.5$, 205.5, 206.5, 207.5, 220.5, 221.5, 222.5, 223.5 with relative abundances that can reach 7% of the base peak.

The high degree of deprotonation of monomer, dimer and trimer, also confirmed by the multiple charged ions, agrees with the elemental analysis of the oxidized polymer and may be due to the cross-linked material. The poor volatility

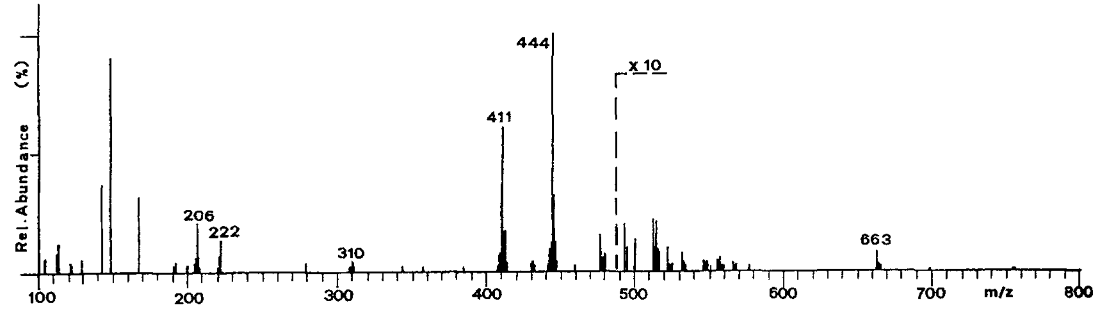

Fig. 7. Mass spectrum of the oxidized compound.

of longer polymer chains and the drastic conditions due to the temperature and the electronic bombardment of the ionic source could explain the absence of peaks in the higher mass range.

### 3.3. *Electric conductivity measurements*

The specific electrical conductivity of the oxidized polymer of TNI was found to be $8.33 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$, of the same order as that of the corresponding polymer of ATNI [9], so indicating that the electrical properties of the latter polymer are not greatly affected by the presence of the aliphatic group in the starting monomer.

The specific conductivity of the neutral polymer of TNI was found to be $3.7 \times 10^{-15}\,\mathrm{S\,cm^{-1}}$, nine orders of magnitude lower than that of the oxidized polymer and comparable with the conductivity of similar undoped materials.

Conductivity and optical spectra of both oxidized and neutral polymer were found to be unchanged for at least a month.

## 4. Conclusions

The electrochemical polymerization of TNI at +2.5–3 V in methylene chloride leads to an oxidized black product. This polymer can be electrochemically reduced to a neutral yellow substance, soluble in several solvents. Both oxidized and neutral polymers are stable molecules. Moreover, from the comparison of electrical conductivity measurements performed on the oxidized products deriving from electrolysis of TNI and ATNI, it was concluded that this property in polyATNI is practically unaffected by the side alkyl groups.

The results of photoconductivity measurements on the neutral polymer will be published and discussed in future papers.

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