

ELECTROACTIVE FILM OF POLYANILINE SUBSTITUTED
WITH THE BENZOTHAZOLE RING

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ABSTRACT

Voltammetric studies of ring-substituted aniline with heterocyclic ring namely 2-(4-aminophenyl)-6-methylbenzothiazole (ABT) were carried out in acetonitrile and acidic aqueous solutions. Potential sweep electrolysis of 0.05M ABT at glassy carbon electrode in CH_3CN containing 0.1M LiClO_4 and 0.05M pyridine produced a polymeric film. The film coated electrode showed an electrochemical response in acidic aqueous solution. The electrical conductivity measurement on pressed pellets of PABT prepared by constant current electrolysis was 3.8×10^{-3} S/cm. Based on IR spectroscopic characterization and electrical conductivity measurement, a polymerization mechanism was proposed.

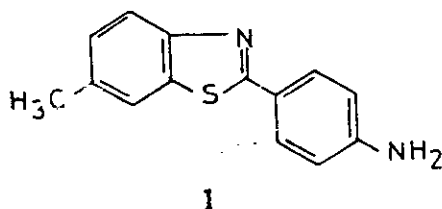
INTRODUCTION

Polyaniline has received considerable attention because of its environmental stability [1]. Substituted anilines with alkyl [2,3] and aryl [4] groups on the aromatic ring and with

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alkyl [5,6], benzyl [7,8] and aryl [9,10] substituents on the nitrogen have been polymerized. The introduction of alkyl groups on the polymer backbone changed the electronic state and stability of the resulting polymer as observed before for alkyl substituted polyaniline [2,7].

In this paper, it is aimed to study the formation of an electroactive film of substituted ring aniline with heterocyclic benzothiazole ring namely 2-(4-aminophenyl)-6-methylbenzothiazole (I) in order to investigate the effect of substitution on the solubility, electroactivity and conductivity of the resulting polymer.



EXPERIMENTAL

Cyclic voltammetry (CV) was carried out using Cypress computer measuring system for electrochemical analysis model CYSY-1B. Current-Voltage curves were recorded on Hewlett-Packard model 7440A. Analytical cell model C-1A (Bioanalytical system) was used together with glassy carbon electrode (3mm. dia.) as working electrode, a platinum counter electrode and Ag/AgCl as reference electrode. Constant current electrolysis (CCE) was carried out using a stabilized current

source model NTN700 M-200 (FuG, Rosenheim) modified as potentiostat. Undivided beaker cell (50ml) equipped with graphite anode (21 cm^2) and Pt cathode was used. IR spectra were recorded on a Perkin-Elmer 2380. Two probe conductivity measurements were carried out on pressed pellets using a Keithley electrometer (Model 160B) and a Keithley multimeter (Model 1160B).

2-(4-Aminophenyl)-6-methylbenzothiazole, lithium perchlorate and acetonitrile were obtained from Aldrich Co. and used without further purification. Aqueous solutions were prepared from distilled water.

Poly 2-(4-Aminophenyl)-6-methylbenzothiazole Film Formation

Poly 2-(4-Aminophenyl)-6-methylbenzothiazole (PABT) films were prepared on glassy carbon electrodes by potential-sweep electrolysis using the analytical cell used before for CV. The PABT films were produced by sweeping continuously between 0 mV and 1200 mV vs Ag/AgCl at a scan rate of 100mV/sec in CH_3CN containing 0.1M LiClO_4 , 0.05 M pyridine and 0.05M ABT monomer. The film coated electrodes were subsequently rinsed thoroughly and used for further electrochemical measurements.

Constant current polymerization (CCP) of ABT

0.05 M of ABT was dissolved in 50 ml CH_3CN containing 0.1M LiClO_4 and 0.05M pyridine and CCP was carried out at 50 mA with continuous stirring and under N_2 atmosphere, at room temperature. Glassy carbon electrode was used as anode and Pt

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as cathode. The solution turned from faint brown to dark turbid brown. After 8 hours of polymerization, the precipitated powder was filtered and washed several times with CH_3CN until the filtrate became colorless. The collected polymer was used for IR and electrical conductivity measurements.

RESULTS AND DISCUSSION

Cyclic Voltammetry in acetonitrile-pyridine and Film Formation

Fig. (1) shows a typical cyclic voltammograms of 0.05M ABT at glassy carbon electrode in CH_3CN containing 0.1M LiClO_4 and 0.05M pyridine. The electrode potential was swept continuously at a rate of 100mV/sec between 0mV and 1200mV vs Ag/AgCl. The monomer electrooxidized irreversibly in one anodic peak at 990mV (from the first potential scan). On subsequent scans, the anodic peak shifted to less positive potentials with decrease in the magnitude of the peak currents due to the blocking of the electrode surface by a growing barrier film.

Cyclic Voltammetric Response of the Polymer Films

After 50 scans, the electrode was rinsed thoroughly before it was transferred to a solution of 1.0 M HCl. Figure 2 shows the typical cyclic voltammetric response of the film in the potential range of 0 mV to 900 mV at different scan rates (100-300 mV/sec). It is obvious that voltammograms have a broad anodic peak at about 720 mV and two cathodic peaks at

580–595 mV and 350–380 mV. The anodic peak currents are almost equal the sum of the two cathodic peak currents ($i_{pc1} + i_{pc2}$). At high scan rate (300mV/sec), the film shows two overlapping oxidation peaks at about 600mV and 750 mV. The first oxidation peak can be attributed to the oxidation of the amine nitrogen and the second peak to the oxidation of another amine group via disproportionation mechanism. Similar results have been reported for poly(diphenylamine [8] and poly(3-methoxydiphenylamine) [12].

The relation between the scan rate v and the redox peaks (i_{pa} and i_{pc}) is shown in Fig.3. This $i_p - v$ linear plot is characteristic for thin polymer films with surface-attached redox species [13].

Cyclic Voltammetry in 1M HCl

Fig.4 shows a typical cyclic voltammograms of 10^{-3} MABT (due to the limited solubility) at glassy carbon electrode in 1.0M HCl in the potential range of 100 mV to 1200 mV at a scan rate of 100 mV/sec. The first scan shows one anodic peak at 870 mV and two cathodic peaks at 562 mV and 354 mV. On the second scan, the anodic peak shifted to a more positive potentials with decrease in the peak current and the two cathodic peaks shifted to more negative potentials. The first cathodic peak current decreased while the second one increased. After ten scans, the anodic peak disappeared completely while the new peak shifted to less positive potential and there was only one cathodic peak at 260 mV which increased in the peak current. After 50 scans, the electrode showed no response in both aqueous and non-aqueous media. This

may be attributed to the low concentration of the ABT monomer where reducing the concentration of the monomer in the solution reduces the conductivity of the product [14].

IR Spectroscopic Characterization and Electrical Conductivity Measurement

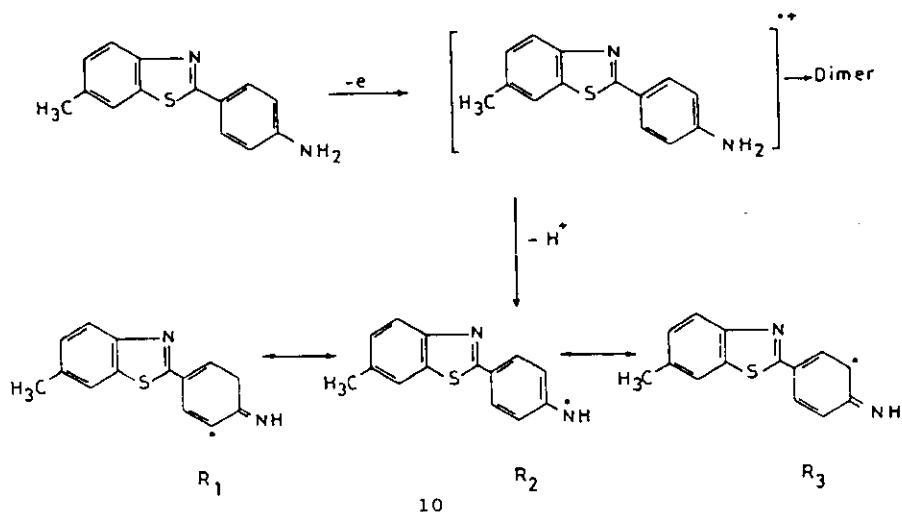
The IR spectrum of the obtained polymer has absorption peaks at 3300–3500 cm^{-1} (NH stretching), 1670–1680 cm^{-1} (C=N bond) and 1300, 1270 cm^{-1} (secondary aromatic amines). This agrees with published work on polyanilines which suggests that polymerization occurs via the formation of C=N=C and C-NH-C bonds [12,15–18].

The electrical conductivity measurement on pressed pellets of PABT was 3.8×10^{-5} S/cm. Typical values of the conductivity of polyanilines [19–21] are ranging between 10^{-1} to 10^{-3} S/cm. The decrease in the conductivity of PABT compared to polyanilines has been observed in the case of alkyl ring-substituted polyanilines [4]. The presence of substituents may have induced some ring twisting with subsequent reduction in π - π conjugation in the polymer chains, destabilizing the polysemiquinone radical cation forms [22]. In addition, the presence of substituents also leads to poor interchain contacts by keeping the polymer chains away from one another, so reducing the probability of charge carrier hopping [4].

2-(4-Aminophenyl)-6-methylbenzothiazole Polymerization Mechanism

Based on the foregoing results, it appears that the anodic oxidation of ABT follows the polymerization mechanism

proposed for the primary aromatic amines [23-28]. The ABT is oxidized to the cation radical (ABT)^{•+} which suffered a fast irreversible chemical reaction to give the dimer (through the radicals R₁-R₃) as shown in the following scheme.



Since the para position in the phenyl ring of aniline is occupied by benzothiazole ring, then the main coupling of the radical occurs via the ortho positions of the phenyl ring [21] (R₂ and R₃). Other possibilities like coupling in the meta position [15] or cross-linking may also occur.

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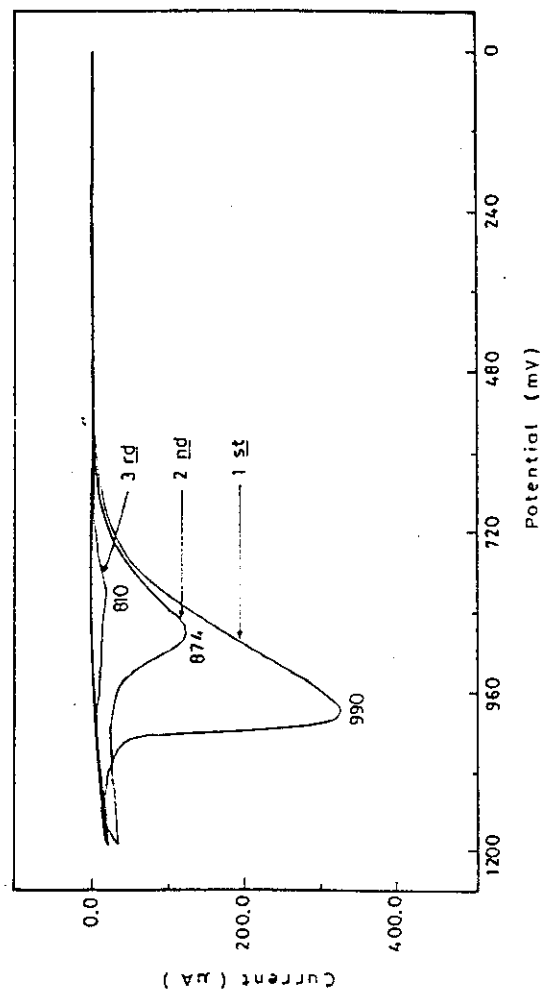


Fig. 1. Cyclic voltammograms of 0.05 M 2-(4-aminophenyl) -
- 6-methylbenzothiozole ($\text{CH}_3\text{CN} + 0.05 \text{ M}$ pyridine + 0.1 M LiClO_4) -
Scan rate = 100 mV/s .

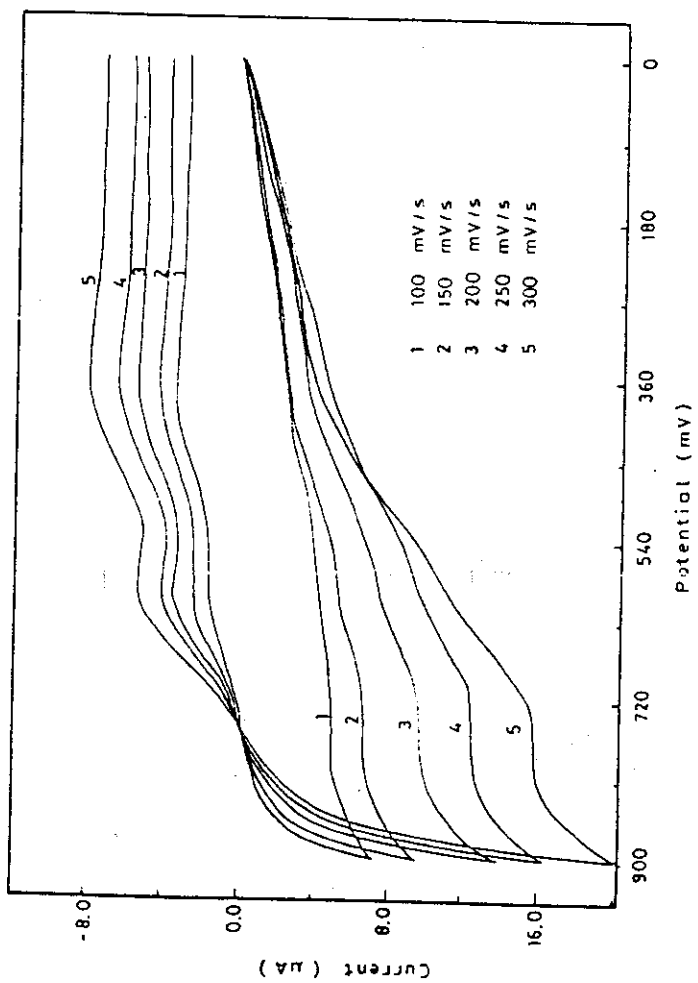


Fig.2. Cyclic voltammograms of glassy carbon electrode covered by PABT films in 1.0 M HCl .

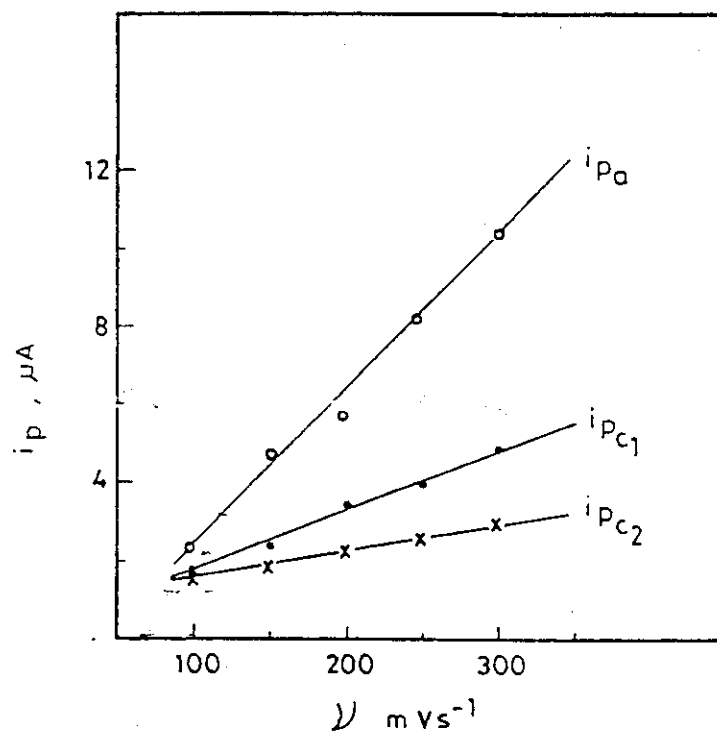


Fig. 3. Dependence of anodic and cathodic currents on potential scan rate -

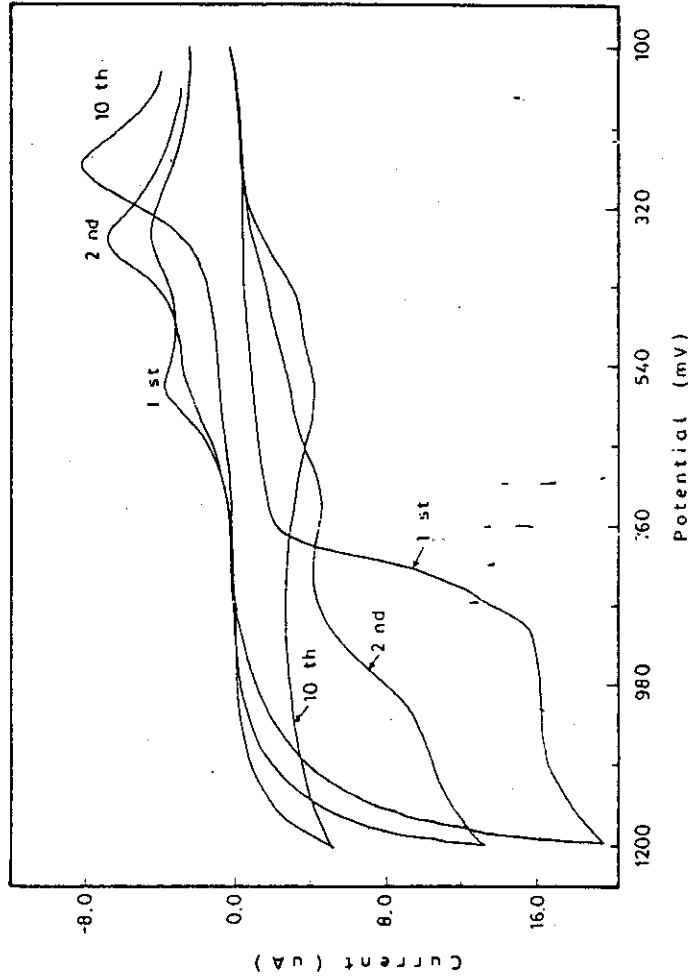


Fig.(4) Cyclic voltammograms of 10^{-3} M 2-(4-aminophenyl) - 6-methylbenzothiazole in 1.0 M HCl. Scan rate = 100 mV/s .

فيلم نشط كهروكيميائيا من البولى انيلين ذو مجموعة بديله من حلقة الثيازول

مجدى عبد العظيم

قسم الكيمياء - كلية العلوم - جامعة المنوفية

تم اجراء دراسات حلقية لمشتق الانيلين والمسمى ٢- (٤-امينوفينيل) -٦-
ميثيل بنزوثيريازول فى الاسيتونيتريل والمحتوى على البيريدين وفى المحاليل المائية
الحمضية . تم تكوين فيلم بوليمرى على سطح القطب الكربونى الزجاجى باستخدام
التحليل الجهدى المسحى. الفيلم المتكون اظهر نشاط كهروكيميائى فى الاوساط المائية
الحمضية. التوصيل الكهربى للاكراص المضغوطة من هذا البوليمر كان
٣٨ x ١٠^{-٥} سيمنز /م.م.

اعتمادا على قياسات الطيف تحت الحمراء والتوصيل الكهربى تم اقتراح نسق
لتوضيح ميكانيكيه البلمره.