

Electrochemical Behaviour of Electroactive / Conductive Poly (α - naphthylamine) in Aqueous Media

Key Words:

electropolymerisation, conductive polymer, poly (α - naphthylamine)

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ABSTRACT

The electroactive poly (α - naphthylamine) was prepared in 0.2 M perchloric acid solution by sweeping potential at the range of -0.5 to $+0.6$ V/vs SCE, on the surface of various solid electrodes such as Pt disk, Au disk, Gc disk and Pt foil (0.5 cm^2).

Electrochemical behaviour was characterized during polymer chain growth and after chain formation by cyclic voltametry. The effects of temperature, the nature of the working electrode, and the sweeping rate of applied potential were studied during the electropolymerisation of the monomer.

INTRODUCTION

The electropolymerisation of mononuclear aromatic amines, such as aniline and their derivatives has received a great deal of attention [1 - 3] due to the attractive behaviour of these conducting polymers. However, these types of studies are scarce for poly nuclear aromatic amines.

Some aspects of electropolymerisation of α - naphthyl amine, ArNH_2 have been reported in eutectic mixture, $\text{NH}_4\text{F}/2.3 \text{ HF}$ over Au electrodes [4], and in acetonitril - pyridine media over graphite electrodes [5].

In previous papers, the electrochemical oxidation of ArNH_2 has been reported in different non-aqueous solvents as well as various experimental conditions [6 - 7].

In this work we report the synthesis of a thin film electroactive conductive poly (α - naphthylamine) in perchloric acid media over different electrodes such as: Pt, Au and Gc. The electrochemical behaviour of polymer during chain growth and after formation is also characterized by cyclic voltametry. At the same time, the effects of temperature, the nature of the working electrode, sweeping rate and applied potential during the electropolymerisation of the monomer have been studied.

EXPERIMENTAL

Commercially available α - naphthyl amine, Merck p. a, was sublimated at 40°C under reduced pressure and kept under vacuum (m. p = 50°C). The lithium perchlorate p. a, Fluka, was recrystallized several times from distilled water and finally dried under vacuum at 200°C for 3 days. Perchloric acid (Fluka) was used without further purification.

The water was distilled in the presence of KMnO_4 in alkaline medium and then distillation was repeated.

For the formation of a thin film of the polymer, an aqueous solution of 0.2 M HClO_4 and 5×10^{-3} M ArNH_2 was prepared. The solution was purged with nitrogen in order to remove any trace of oxygen. The potentials were measured vs saturated calomel electrode (SCE). A conventional compartment thermostated pyrex cell with double walls was used for the electropolymerisation and study of the film formation in the solution.

The working electrodes were platinum, Gc and Au disks, and platinum foil (0.5 cm^2). The electrodes were washed before each measurement in concentrated nitric acid and polished mechanically with alumina powder. The auxiliary electrode was platinum wire and a standard calomel electrode was used as a reference electrode.

Poly (α -naphthyl amine) was grown on different electrodes and potential scanned in the range of -0.5 to $+0.6$ V/vs SCE. After polymerisation, the anode was rinsed with corresponding acid with the same concentration, and transferred to another three electrode cell, containing 0.2 M HClO_4 . Cyclic voltametry experiments were performed with Polarecord E506 combined with VA- Scanner E612 and 7015 A X-Y recorder Hewlett Packard.

RESULTS AND DISCUSSION

The thin film of the polymer was grown on the surface of the working electrode until thirty sweeping potential. Then the electrode was rinsed with 0.2 M HClO_4 and transferred to another three electrode cell containing 0.2M HClO_4 . Cyclic voltamogram of polymers was performed over electrodes (i. e. Gc, Pt, Au disks and Pt foil) in the range of -0.5 to $+0.6$ V/vs SCE at 35°C and a sweep rate of 100 mV/s (Figure 1).

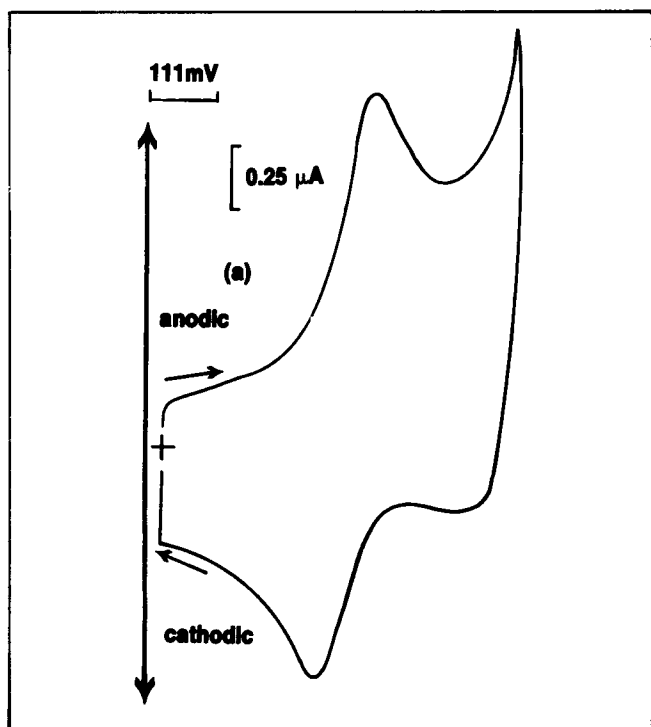


Figure 1 (a): C.V of poly (α - naphthylamine) foil Pt electrode, $T = 35^\circ\text{C}$, $SW = 100\text{ mV/sec}$, potential range = -0.2 to $+0.6\text{ V/ vs SCE}$.

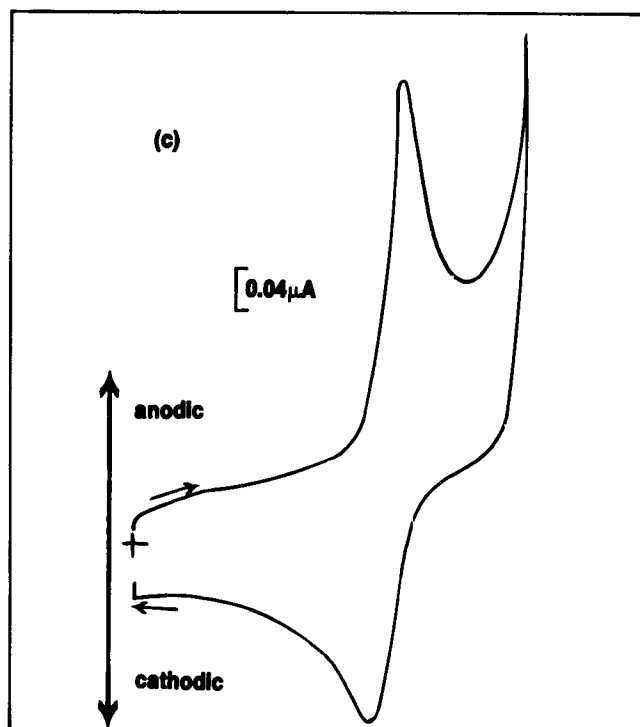


Figure 1 (c): C.V of poly (α - naphthylamine), Gc electrode, $T = 35^\circ\text{C}$, $SW = 100\text{ mV/sec}$, potential range = -0.5 to $+0.6\text{ V/ vs SCE}$.

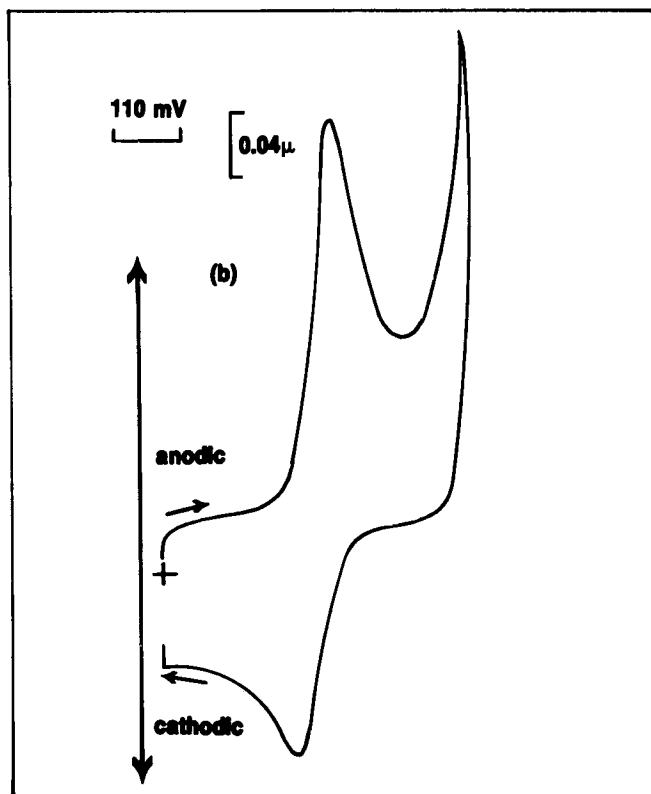


Figure 1 (b): C.V of poly (α - naphthylamine) disk Pt electrode, $T = 35^\circ\text{C}$, $SW = 10\text{ mV/sec}$, potential range = -0.2 to $+0.6\text{ V/ vs SCE}$.

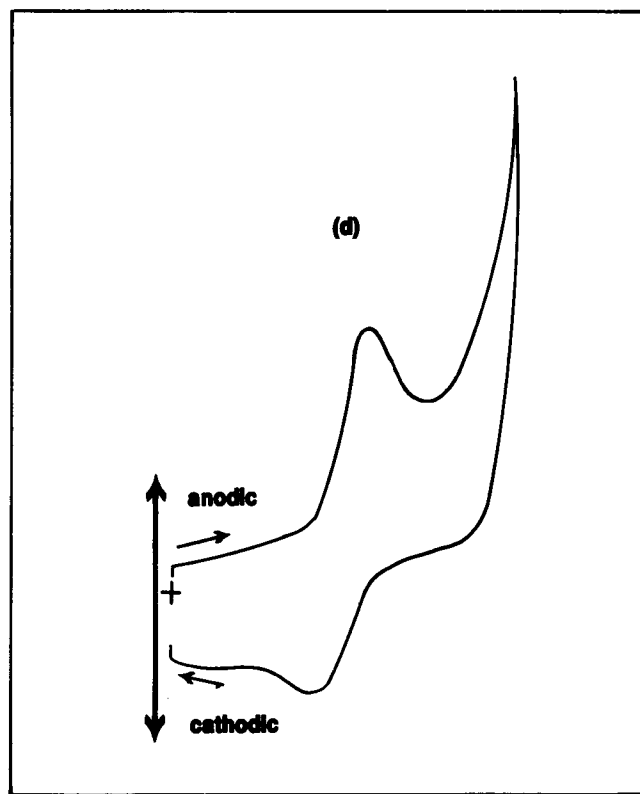


Figure 1 (d): C.V of poly (α - naphthylamine) disk Au electrode, $T = 35^\circ\text{C}$, $SW = 100\text{ mV/sec}$, potential range = -0.2 to $+0.6\text{ V/ vs SCE}$.

From Figure 1 it is clear that for all polymerisations, the peaks of oxidation and reduction are reversible. When platinum disk is used, E_{pa} appears at 0.249 V/vs SCE and E_{pc} at 0.140 V/vs SCE. By using platinum foil, E_{pa} is 0.271 V/s SCE and E_{pc} is 0.162 V/vs SCE and with Au disk, E_{pa} and E_{pc} are 0.296 V/vs SCE and 0.14 V/vs SCE, respectively.

For investigation on the effect of electrode nature, the chain growth of polymer is studied over different electrodes with the same conditions. In any case, after washing the deposited polymer with the same acid, the electrode was placed in perchloric acid with the same concentration. With various sweeping rates, cyclic voltamogram was performed for these polymers. The I_{pa} is plotted vs sweeping rate as shown in figure 2. These plots indicate that platinum foil is the best working electrode, owing to its ability for formation of a thin film polymer with high conductivity.

For studying the influence of sweeping rate on the chain growth of poly (α -naphthylamine), the Gc electrode is used. In the same condition with sweeping rates of 30, 50, 70, 90, 100 and 200 mV/s the polymer was deposited on Gc electrode after the thirtieth sweep. The plot of I_{pa} vs sweeping rate shows that the maximum current due to high conductivity of formed polymer film is obtained in the sweeping rate of 100mV/s (Figure 3).

Figure 3 indicates that in the high sweeping rates, the time required for multisteps eletropolymerisation process is not favorable, and this prevents the favorable configuration of active species for chain growth of polymer. As a result, a polymer with disordered structure is formed on the electrode surface.

The comparison between cyclic voltamograms of poly (α -naphthylamine), prepared at the temperatures of, -2, 10, 15, 20, 25, 30, 35, 40, 50 and 60°C shows that the electrical conductivity of poly (α -naphthylamine) film prepared at low temperature is small and as the temperature is increased the conductivity and electro-activity increase.

As the temperature increases, the growth of polymer film and the electrical conductivity both decrease. The melting point of α -naphthylamine is 50°C and the prepared polymer film at this temperature shows a decrease in electrical conductivity which cannot be accounted for.

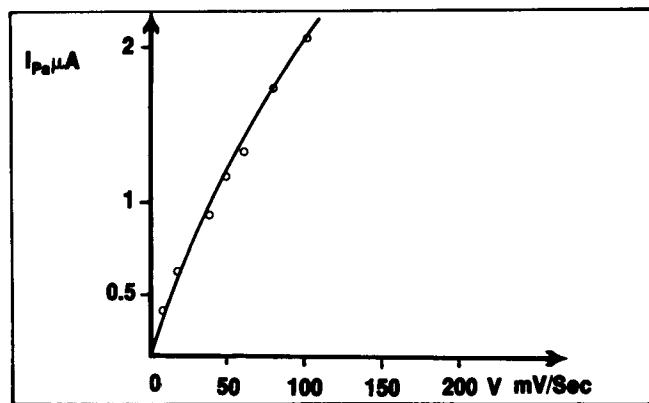


Figure 2 (a): The plot of I_{pa} vs sweeping rate for the poly (α -naphthylamine) film, deposited on Pt electrode.

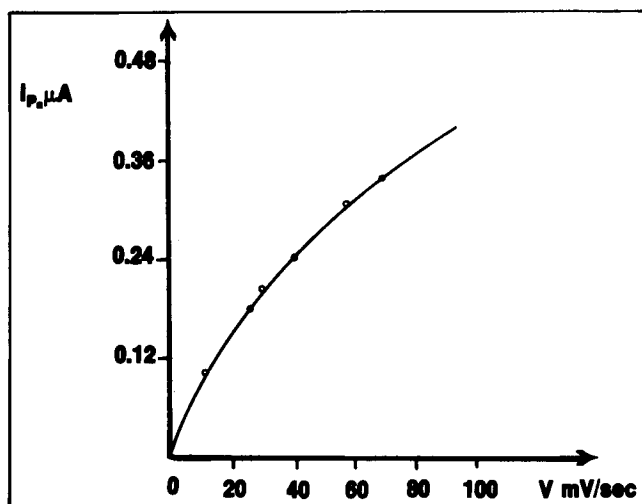


Figure 2 (b): The plot of I_{pa} vs sweeping rate for the poly (α -naphthylamine) film, deposited on Gc electrode.

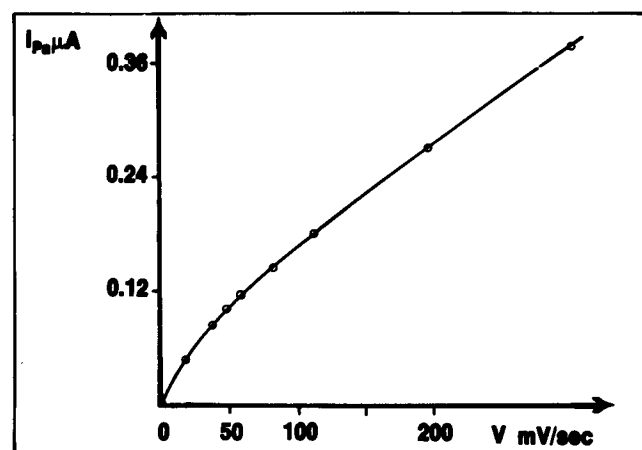


Figure 2 (c): The plot of I_{pa} vs sweeping rate, for the poly (α -naphthylamine) film deposited Au electrode.

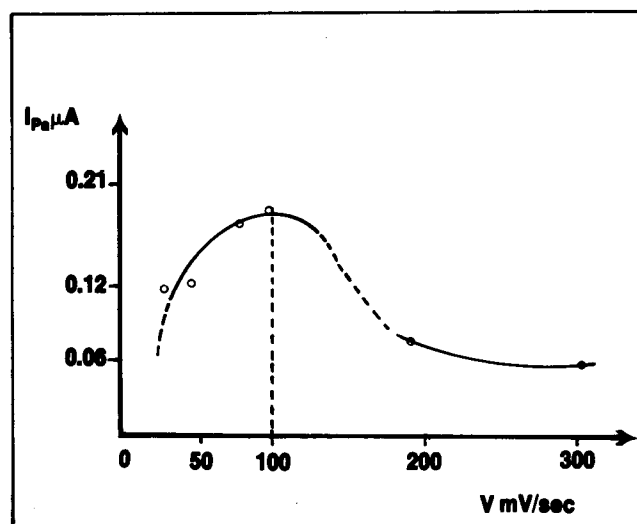


Figure 3: The plot of I_{pa} vs sweeping rate for thin film of poly (α -naphthylamine) prepared at various sweeping rates.

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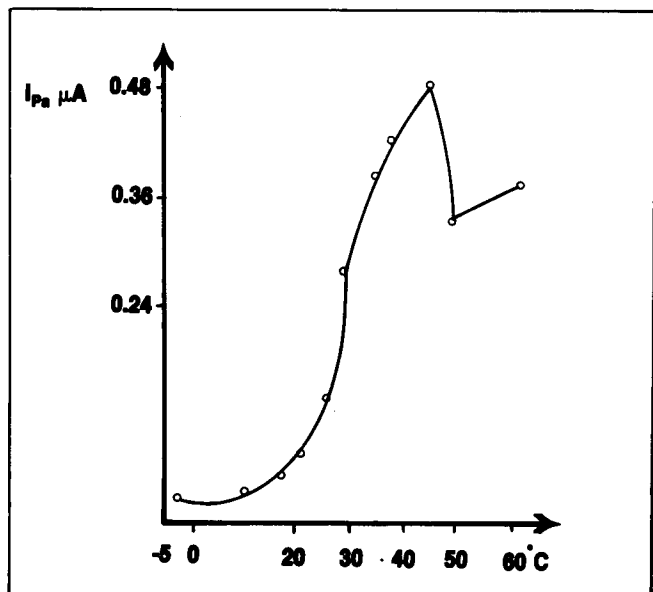


Figure 4: The plot of I_p vs temperature for thin film of poly (α - naphthylamine) prepared at various temperatures.