

ELECTROPOLYMERIZATION OF ANILINE AND SOME OF ITS DERIVATIVES

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The effect of substitution on the aromatic ring of aniline and in its amino group on the potential of polymerization in aqueous medium and on the charge passed during polymerization was studied. The formation of polymer films on the working electrode and their electrochromic changes were also examined. From the electro-oxidation of aniline, the number of reversible and irreversible steps, the number of electrons exchanged and the type of oxidation mechanism were found. The thickness of a single layer of polyaniline, formed by cycling the potential in the range -0.2 V, $+1.4$ V (vs SCE) at a polarization rate of 5 mV/s, was estimated considering the oxidation mechanism of aniline. The electrochemical behaviour of aniline in anhydrous acetonitrile medium was also studied. It was found by blocking the *m*- and *p*-positions in aniline by a methyl substituent that polymerization of aniline occurs through the *p*-position. The porosity of the polymer films was estimated from the diffusion coefficient values for $1 \cdot 10^{-3}$ M $K_3[Fe(CN)_6]$ in 0.1M-KCl calculated from the Randles-Ševčík equation for measurements on Pt electrodes with a polymer film, compared with the tabulated values for a bare Pt electrode.

The electrochemically initiated polymerization of organic substances has recently been widely used for the preparation of polymers with interesting properties^{1,2}. These materials have been used as electrodes and electrolytes in miniature and classical current sources³⁻⁵, have been used in the manufacture of optical displays based on electrochromic phenomena and have been used for material protection in corrosion engineering⁶, for example in the manufacture of integrated circuits.

Of the wide range of organic substances that are capable of electropolymerization, aniline has some exceptional properties. In particular, it can undergo electro-oxidation in aqueous medium and its polymeric products are resistant to oxygen, acidic and alkaline media. Depending on the reaction medium, its oxidation occurs in one or two steps and structural changes in the material are accompanied by visible colour changes⁷. The electroactivity of polyaniline was studied for products obtained from both aqueous and nonaqueous media, including melts^{8,9}. Although polyaniline has been widely studied, its oxidation mechanism has not yet been completely elucidated. The clarification of the mechanism of the electrochemical oxidation of aniline and polyaniline could follow from structural changes in the monomer, i.e. substitution changes on the aromatic ring and in the amino group.

EXPERIMENTAL

Chemicals

Aniline was repeatedly distilled under reduced pressure. The contents of some impurities were determined by mass spectroscopy to be less than 0.5%. Acetonitrile was purified in the recommended manner¹⁰, i.e. by stepwise refluxing for several hours with 10% aqueous solution of KOH, Al₂O₃ and P₂O₅. The final acetonitrile fraction was collected at a temperature of 81.5°C ($n_D^{20} = 1.3440$). Less than 3% impurities were found by mass spectroscopy. Redistilled acetonitrile was stored over a molecular sieve in a dark bottle in a refrigerator. *m*-Toluidine, *p*-toluidine, *N*-ethylaniline and *N,N*-diethylaniline were redistilled. The LiClO₄ employed was anhydrous.

Apparatus

Experiments were carried out in an electrolytic vessel with separated cathodic and anodic spaces in a three-electrode arrangement with a platinum working electrode (2.315 cm²), platinum auxiliary electrode and saturated calomel reference electrode, connected with the electrolytic vessel by a Luggin capillary. During measurements in acetonitrile, the reference electrode was connected with the electrolytic vessel by a salt bridge containing 0.3M-LiClO₄ in acetonitrile. Oxygen was removed from the solution by bubbling with nitrogen which was passed through a chromous salt solution over zinc amalgam.

The cyclic voltammograms were recorded using a PA3 polarographic analyzer with a 4105 X-Y recorder (Laboratorní přístroje, Prague). Where not stated otherwise, the electropolymerization of the substituted anilines was studied by cycling the potential in the range -0.2 V, +1.4 V vs SCE at a polarization rate of 5 mV/s in 0.05 mol l⁻¹ monomer solutions with a concentration of 0.30M-NaClO₄ as an inert electrolyte and 3M-HClO₄. Polymer films strongly adhering on the electrode were removed by ignition in a flame. All the potentials given are related to the saturated calomel electrode.

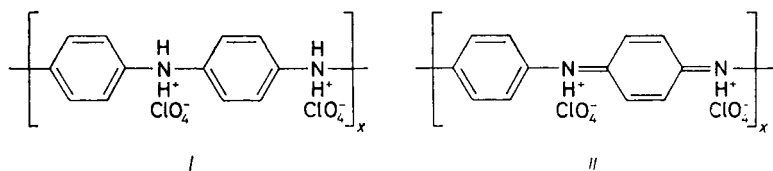
RESULTS AND DISCUSSION

Electro-oxidation of Aniline

Fig. 1 depicts the voltammograms for the first and fifth cycles. A steep wave for the oxidation of aniline appears in the first cycle, beginning at 0.84 V. In subsequent cycles, the redox properties of the polyaniline film are evident, accompanied by electrochromic changes. The green/blue electrochromic change occurs at a potential of +0.34 V and blue/black at +0.62 V. The electrochromic changes are connected with the increasing degree of oxidation of aniline black, when the benzene ring of polyaniline is converted to a quinoid ring, which contains suitable chromophores. With the cycling going on, the colour changes in the polyaniline film become less sharp since the polymerization of aniline progresses, the film grows and becomes black (i.e. aniline black).

Two oxidation and two reduction peaks can be distinguished on the cyclic voltammogram in the potential range 0-0.65 V. The height of the first oxidation peak

increases with increasing number of cycles. As the polarization rate increases, the corresponding reduction peak completely disappears, indicating the presence of a kinetically-controlled step which is decisive for this electrode reaction. Because of the high acidity of the reaction medium, the most probable chemical step is complete protonation of all the nitrogens in the polyaniline chain. It follows from Fig. 1 that the first oxidation step is irreversible. The chemical formulae depict two types of units that are repeated in the polyaniline structure: the completely reduced, completely protonated basic unit of polyaniline (I) and the completely oxidized, completely protonated basic structural unit of polyaniline (II)¹¹, as they may correspond to the first oxidation step.



The second peak in the cyclic voltammogram is reversible, as can be seen from Fig. 1 and also from the dependence of I_p on $v^{1/2}$, which is linear in a wide range of $v^{1/2}$ values. These dependences also indicate that the current is diffusion-controlled. The number of electrons exchanged in the reversible step was found from the relationship $|E_p - E_{p/2}| = 59/n$, yielding values of 1.03 and 0.95. The peak potentials E_p and

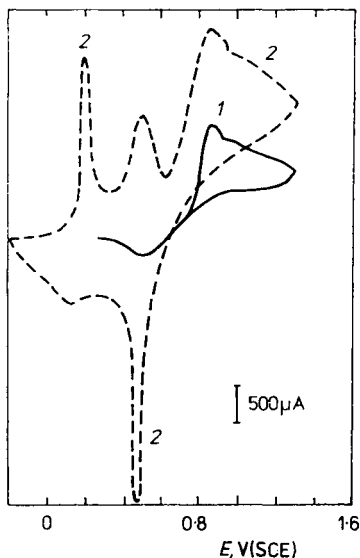
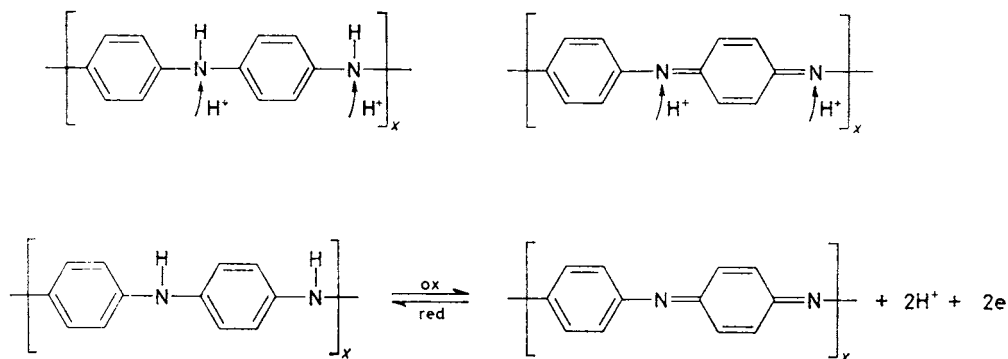


FIG. 1

Cyclic voltammogram of 0.05M aniline at a Pt electrode in 3M-HClO₄ with 0.3M-NaClO₄ as an inert electrolyte; polarization rate 5 mV/s; 1 1st cycle, 2 5th cycle

$E_{p/2}$ are 505, 448 and 460, 398 mV, respectively. The average current ratio is $I_p^A/I_p^C = 0.98$.

In conclusion, the oxidation of polyaniline occurs through a CE mechanism that can be depicted by the scheme involving protonation of the nitrogen and electro-oxidation of polyaniline (Scheme 1).



SCHEME 1

The number of oxidation steps of the polymer depends on the monomer concentration. In more concentrated solutions (0.15M monomer), the second pair of peaks on the cyclic voltammogram of aniline contains a small peak following the oxidation peak. At the same potential, a small peak then appears, preceding the corresponding reduction peak. The agreement of these peak potentials in regard to aniline concentration indicates that the oxidation products are probably adsorbed on the electrode surface¹².

The dependence of the height of the polymerization current (the third peak in Fig. 1) on the number of cycles is linear, i.e. in each cycle the film on the working electrode increases by a regular increment. On the basis of the Faraday Law and the simplifying assumption that the densities of aniline and polyaniline are similar, it was calculated that the film on the electrode increases by about 80 nm in each cycle.

From the analysis of the oxidized form of polyaniline by IR spectroscopy it was found that the polymer contains mainly benzene rings. A small vibration was also found corresponding to the —C=C— group in the quinoid structure ($1\,780\text{ cm}^{-1}$). A weak vibration was found for the —N=N— group ($1\,160\text{ cm}^{-1}$), which can also be present in the polymer chain in a case of a suitable combination of radical cations. The strongest vibration (symmetrical valence, antisymmetrical valence) was found for the N—H group (double band at $\sim 3\,500\text{ cm}^{-1}$).

To clarify the role of protons in the electro-oxidation of aniline, this reaction was studied in anhydrous acetonitrile. It can be seen from the cyclic voltammogram

(Fig. 2) that formation of the aniline radical cation in acetonitrile medium is more difficult, as the $C_6H_5NH_3^+$ cation capable of oxidation and subsequent polymerization is not allowed to be formed in this medium. A purple oxidation product is formed at a potential of +0.82 V on the working electrode, but it is dissolved when the potential sweep is reversed and it is not formed during subsequent oxidation. The redox polyaniline response and electrochromic changes observed for aniline in aqueous medium are completely lacking on the cyclic voltammogram. Precise addition of water to the electrolyte (5 wt. %, 10 wt. %) and of perchloric acid (with a final concentration of 0.15 mol dm^{-3}) led only to changes in the shape of the cyclic voltammogram and to a slight indication of a polyaniline redox response in the potential range expected. Thus, the concentration of H^+ ions was not sufficient for attaining the expected redox behaviour of polyaniline in acetonitrile.

Electro-oxidation of *m*-toluidine and *p*-toluidine. It follows from the cyclic voltammogram of *m*-toluidine (Fig. 3) that polymerization of the monomer occurs at a potential of +1.26 V. The very large peak at a potential of +0.92 V does not correspond to polymerization apparently and is absent in subsequent cycles. The shape of the cyclic voltammogram is very similar to the cyclic voltammogram of aniline, including the irreversible and reversible peak and the colour changes. Cyclic potential changes in the range -0.2 V , $+1.4 \text{ V}$ produce electrochromic changes that are very reminiscent of those for polyaniline. The light green/dark green colour change at $E = 0.28 \text{ V}$ corresponds to the reduced form of polytoluidine and the dark green/blue-black change at $E = 0.60 \text{ V}$ corresponds to the oxidized form of polytoluidine. The dependence of I_p on $v^{1/2}$ is almost linear for the second peak and the number of electrons exchanged is 1.05 and 1.08. The formal αn_a value for the irreversible peak is 0.95. The oxidation mechanism for poly(*m*-toluidine) is similar to that for polyaniline, i.e. of the CE type.

The electro-oxidation of *p*-toluidine (Fig. 4) involves a current increase at a potential of 1.07 V with formation of a coloured oxidation product on the electrode; when the potential sweep was reversed, this film was readily dissolved. Repeated

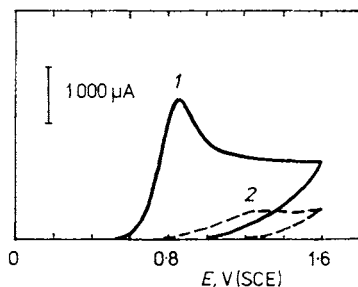


FIG. 2
0.05M aniline at a Pt electrode in acetonitrile with 0.3M-LiClO₄ as an inert electrolyte; 1 1st cycle, 2 5th cycle

cycling in the range from -0.2 V to $+1.4$ V yields practically the same current peak sizes; the slight decrease in the peak height can be attributed to gradual depletion of the solution layer. When the *p*-position in aniline is blocked by a substituent, a polymer layer is not formed on the electrode.

The structural changes in the monomer affect its electrochemical behaviour, since the substituents increase or decrease the electron density in certain parts of the molecule. As the structure of the methyl group is such as to supply electrons to the aromatic ring, it facilitates oxidation of the derivative in the *p*-position; i.e., the oxidation potential of the *p*-derivative is lower than that of the *m*-derivative ($1.07 < 1.26$ V), but polymerization of the *p*-derivative can not progress further on (the suitable combination of radical cations is limited).

Electro-oxidation of N-Ethylaniline and N,N-Diethylaniline

N-Ethylaniline polymerizes at a potential of $+0.95$ V (Fig. 5). The reversible response on the cyclic voltammogram corresponds to an average number of the exchanged electrons of 1.10. It follows from the comparison of the cyclic voltammogram for aniline and N-ethylaniline that replacement of one hydrogen in the amino group of aniline by an ethyl group results in disappearance of one of the peaked responses. Poly(N-ethylaniline) retains its electrochromic properties. The yellow/green-blue change occurs at $E = 0.7$ V, where the yellow film colour corresponds to the reduced form of the polymer and green-blue to the oxidized form of poly(N-ethylaniline).

The replacement of both hydrogen atoms in the amino group by ethyl unfavourably affects the formation of radical cations required for the polymerization. Although

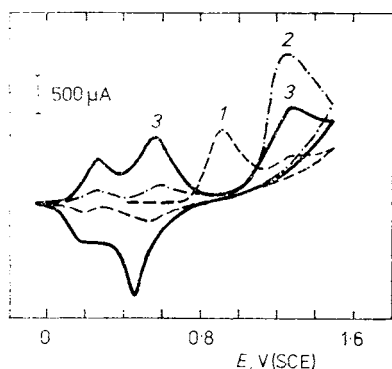


FIG. 3
0.05M *m*-Toluidine, as in Fig. 1: 1 1st cycle,
2 2nd cycle, 3 5th cycle

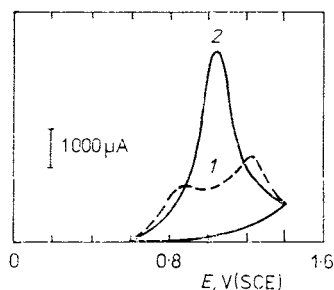


FIG. 4
0.05M *p*-Toluidine, as in Fig. 1; 1 1st cycle,
2 2nd cycle

TABLE I

Parameters studied in the electropolymerization of aniline derivatives (D is the diffusion coefficient for $K_3[Fe(CN)_6]$)

Monomer	Monomer oxidation potential V	Q^+ mC	Film	D $m^{-2} s^{-1}$	Electrochem. and physical properties
Aniline	+0.84	164.4	+	$2.55 \cdot 10^{-11}$	active impermeable
<i>m</i> -Toluidine	+1.27	144.6	+	$1.16 \cdot 10^{-9}$	active permeable
<i>p</i> -Toluidine	+1.07	240.3	—	—	inactive —
N-Ethylaniline	+0.95	912.4	+	$3.98 \cdot 10^{-11}$	active impermeable
N,N-Diethylaniline	+0.94	63.1	—	—	inactive —

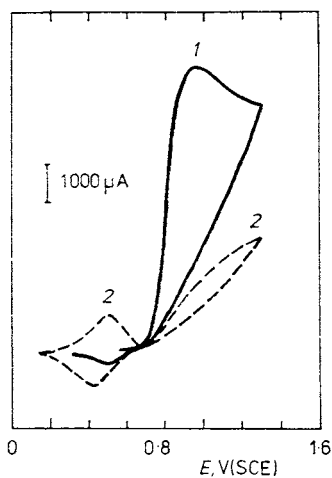


FIG. 5
0.05M N-ethylaniline, as in Fig. 1; 1 1st cycle, 2 5th cycle

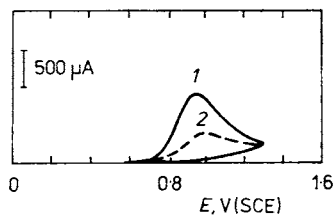


FIG. 6
0.05M N,N-diethylaniline, as in Fig. 1; 1 1st cycle, 2 5th cycle

oxidation occurs at a potential of $E \sim 1.00$ V (Fig. 6), it is not accompanied by visible changes in the vicinity of the electrode. As electropolymerization does not occur in this case, it can be assumed that formation of the radical cation is prevented by the bulky ethyl group and that the hydrogen atoms perform an active role in the electropolymerization process.

Table I lists the experimental results for aniline derivatives and gives the film properties. The concept of permeable, semi-permeable or impermeable is connected with the diffusion coefficient value D for $0.001\text{M-K}_3[\text{Fe}(\text{CN})_6]$ in 0.1M-KCl obtained from the Randles-Ševčík equation for an electrode covered with a polymer film. This value equals $7.63 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for a bare platinum electrode¹³.

The charge Q^+ consumed during polymerization (or oxidation) of the monomer is an orientative value permitting quantitative evaluation of the ability of the monomer to polymerize. It follows from the table that N,N-diethylaniline is least capable of polymerization.

REFERENCES

1. Chandler G. K., Pletcher D.: *The Electrochemistry of Conducting Polymers*. Specialist Periodical Reports, Vol. 10 — Electrochemistry. Royal Society of Chemistry, London 1985.
2. Adamcová Z.: Chem. Listy 81, 673 (1987).
3. Papež V., Mrha J., Novák P., Klápště B.: Chem. Listy 79, 1131 (1985).
4. Říha J., Novák P., Mrha J.: Chem. Listy 80, 113 (1986).
5. Mrha J., Novák P., Říha J.: Chem. Listy 80, 274 (1986).
6. Berry D. W.: J. Electrochem. Soc. 132, 1022 (1985).
7. Watanabe A., Mori K., Iwasaki Y., Nakamura Y., Niizuma S.: Macromolecules 20, 1793 (1987).
8. LaCroix J. Ch., Diaz A. F.: Makromol. Chem. 8, 17 (1987).
9. Genies E. M., Tsintavis C.: J. Electroanal. Chem. 200, 127 (1986).
10. Hofmanová A., Angelis K.: Chem. Listy 72, 306 (1978).
11. Chiang J. C., MacDiarmid A. G.: Synth. Metals 13, 193 (1986).
12. Bard A. J., Faulkner L. R. in: *Electrochemical Methods*, p. 529. Wiley, New York 1980.
13. Dobos D.: *Electrochemical Data*. Akademiai Kiadó, Budapest 1975.

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