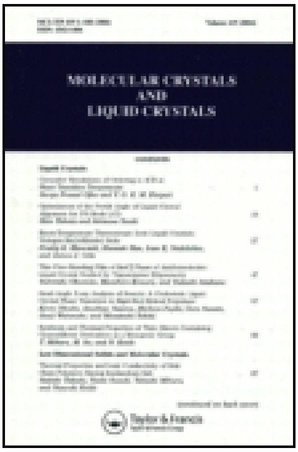

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A Novel Highly Conducting Ring-Substituted Polyaniline

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A NOVEL HIGHLY CONDUCTING RING-SUBSTITUTED POLYANILINE

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Abstract Electrochemical oxidation of 2,5-dimethoxyaniline in 1.0 M $NaHSO_4$ produces a head-to-tail coupled substituted polyaniline with exceptionally low redox potentials (-0.1 and 0.45 V vs SCE). The polymer displays high stability towards oxidative degradation, good solubility in chloroform (30 g/l) and high conductivity (5 S/cm) in the emeraldine state .

INTRODUCTION

After the discovery of the conducting properties of polyaniline (PANI), much work has been devoted to substituted polyanilines aiming mostly to the obtaining of soluble (and hence processible) polymers as PANI itself is hardly soluble. Unfortunately substitution leads generally to a severe decrease of conductivity. We therefore applied to the electropolymerization of 2,5-dimethoxyaniline, in which the presence of two solvating and low-hindrance methoxy substituents was expected to produce a soluble polyaniline with high conductivity.

EXPERIMENTAL

2,5-dimethoxyaniline (DMA) was purified by sublimation. Experiments were performed at 25° C under nitrogen in three electrode cells with 1 M $NaHSO_4$ (pH = 1) as supporting electrolyte. The counterelectrode was platinum and the reference electrode was SCE. The working electrode for cyclic voltammetry was a glassy carbon disc (0.2 cm^2), for electronic spectroscopy a 0.8x2.5 cm indium-tin-oxide (ITO) sheet (ca 80% transmittance, ca 300 ohm/square resistance, from Balzers, Liechtenstein) and for preparative electrolyses a platinum sheet (15 cm^2).

The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator. Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer and IR spectra with a Perkin Elmer 682 spectrometer as reflection-absorption spectra (RAS). Conductivity measurements were performed in-situ with a two-band microelectrode (spacing 6 micrometers) calibrated with poly(3-methylthiophene)[1].

RESULTS AND DISCUSSION

Electrodeposition of the polymer

Cycling of the potential between -0.6 and 0.6 V in 0.1 M DMA produces initially the development of a double redox cycle at 0.1 and 0.3 V, due to the head-to-tail (N-phenyl-paraphenylendiamine) and tail-to-tail (benzidine) dimers respectively[2]. With subsequent cycling, wing cycles at -0.1 and 0.45 V, attributable to the polymer (PDMA), are observed. The stationary current during growth is sigmoidally related with potential with $E_{1/2}$ = 0.45 V, i.e. the potential of the second redox cycle. The maximum current density is 2.4 mA/cm^2, vs 7.5 for PANI under the same conditions. This indicates that PDMA growth occurs from the fully oxidized form of the polymer as for PANI[3]; the rate is not much lower which means that the substituent groups do not oppose high barriers to polymerization.

Bulk polymer was produced by electrolysis of 0.1 M DMA + 1.0 M $NaHSO_4$ at 0.6 V. The solid is washed with 1.0 M $NaHSO_4$ and then either with 0.1 M H_2SO_4 to obtain the acid emeraldine or with water and 1.0 M NH_3 to obtain the base emeraldine. The latter, after dissolving side products and oligomeric species with acetone, appears as a dark blue solid very soluble in $CHCl_3$ (30 g/l).

Characterization of the polymer

Cyclic voltammetry of PDMA-filmed electrode in blank solution displays, beside the redox cycles at -0.1 and 0.45 V, intermediate redox cycles due to incorporated dimeric species. After NH_3 neutralization of the oxidized form, the dimers dissolve in acetone as it appears from the cyclic voltammogram which does no longer display the relevant redox cycles. Neat dimer-free polymer may be produced also directly by cycling under stirring. Fig.1 shows the redox behaviour of the neat polymer film.

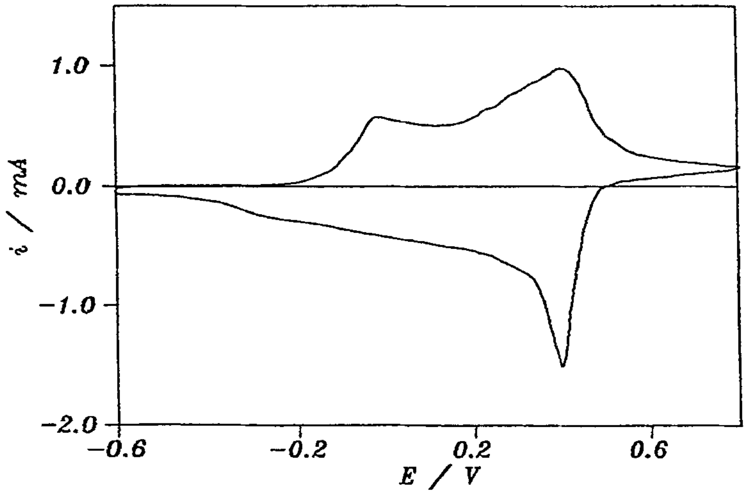

FIGURE 1 Cyclic voltammogram of PDMA deposit in 1.0 M $NaHSO_4$

Films are very stable to oxidation as no degradation is observed up to 0.8 V.

The IR spectrum of DPMA in the neutral state shows the bands of the monomer, with the only exception that of the original bands for CH o.o.p. deformation at 835 and 780 cm^{-1} the latter is absent, which indicates tail-to-tail coupling. In the fully oxidized and compensated state (pernigraniline base) the IR spectrum shows the disappearance of the NH stretching band at 3400 cm^{-1} and the appearance of a strong signal at 1570 cm^{-1}, due to C=N stretch[4].

Spectroelectrochemistry (fig.2) shows that upon oxidation the maximum absorption at 365 nm change to a peak at 450 nm at half-oxidation (emeraldine form) with an isosbestic point at 400 nm. Further oxidation to the pernigraniline form causes the decrease of the band at 450 nm and the appearance of a broad band at ca 800 nm with a second isosbestic point at 512 nm.

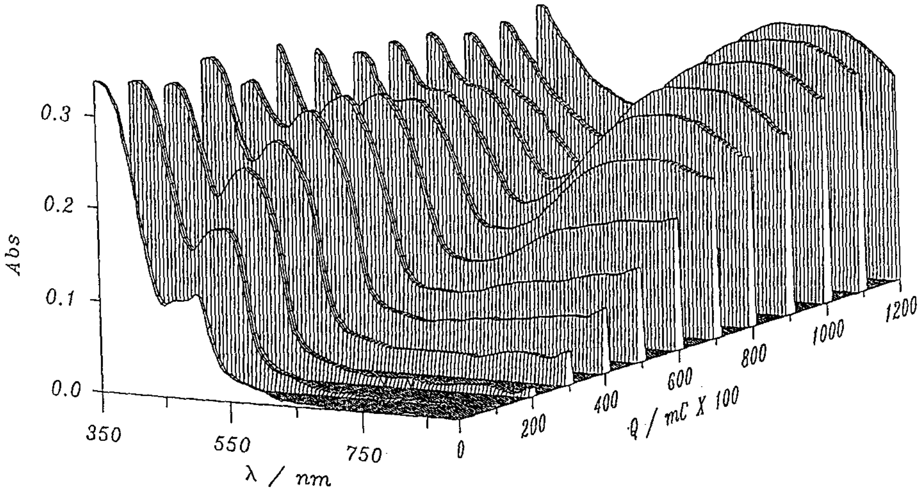

FIGURE 2 Spectroelectrochemistry of PDMA in 1.0 M $NaHSO_4$.

In-situ conductivity (fig.3) indicates that the polymer becomes conducting at the intermediate (emeraldine) state and then insulating again at the pernigraniline state, with a maximum conductivity of 5 S/cm at the intermediate potential of 0.2 V. Conductivity is higher than that of substituted polyanilines and comparable to that of PANI itself.

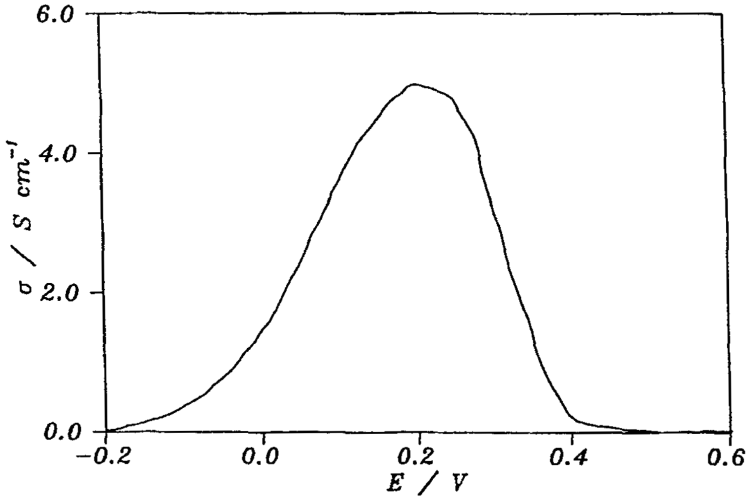

FIGURE 3 In-situ conductivity of PDMA in 1.0 M $NaHSO_4$.

CONCLUSIONS

Electroxidation of 2,5-dimethoxyaniline in 1.0 M $NaHSO_4$ produces the easy deposition of the head-to-tail coupled polyaniline. This is the second reported disubstituted polyaniline, after the 2,5-dimethylsubstituted polymer[5], which is soluble but low-conducting (ca 10^{-5} S/cm). Due to the presence of two electron-rich substituents, the polymer is oxidized at low potentials and is stable in the fully oxidized form. Furthermore the double substitution gives it high solubility without depressing the conductivity, which may be attributed to the low steric hindrance of the methoxy groups, as previously observed in polythiophenes[6]. For all these properties the use of PDMA is expected to give significant improvements to the performances of polyaniline in all its proposed and possible future applications.

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