

ORIGINAL PAPER

Joëlle Rault-Berthelot · Marie Madeleine Granger

Anodic oxidation of 2-aminofluorene in CH₂Cl₂ + 0.2 M Bu₄NBF₄: electrochemical behaviour of the derived oxidation products

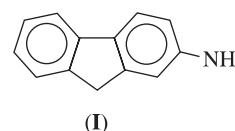
Received: 8 January 1998 / Accepted: 21 September 1998

Abstract The physicochemical properties and electrochemical behaviour of products obtained by anodic oxidation of 2-aminofluorene in CH₂Cl₂ + 0.2 M Bu₄NBF₄ are presented together with the oxidation conditions.

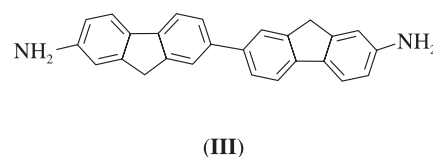
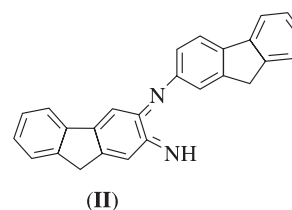
Key words Electropolymerization · Conducting polymer · Polyaminofluorene · Anodic oxidation

Introduction

Since 1985, our group has been interested in the anodic polymerization of fluorene derivatives [1]. At the beginning, we demonstrated that polymers derived from fluorene [2, 3], 9-substituted or 9,9-disubstituted fluorenes [4] are electroactive materials possessing p- and n-doping process. Their uses as electrochromic materials, electrode modifiers [5–7], in bi- or trilayer devices [8] or as complexing materials [9, 10] were developed. Later on, the anodic polymerization of fluorenylidene derivatives was studied [11–13]. These polymers were substituted by electron-donor [14] or electron-withdrawing groups [13]. When the substitution was performed by cyano group(s), these matrices were demonstrated to present affinity towards metallic cations and metal-polymer composites were used as efficient electrode modifiers for electrocatalytic reactions [15]. Our interest was also focused on the anodic behaviour of 2-substituted fluorenes, leading to sequential polyphenylene-fluorene [16] or to extended polyarylenevinylenes [17]. This paper deals with the anodic behaviour of the 2-aminofluorene (I).



Previous work on this compound was described by Japanese researchers in 1979 [18] and by American workers in 1985 [19]. The two groups studied the oxidation of I in acetonitrile medium. They showed that I oxidation presents two oxidation waves: the first one of the neutral species and the second one of its protonated form. They demonstrated the formation of a dimer. The Japanese spoke of an *ortho*-semidine-type dimer II resulting from C–N coupling, and the Americans of a difluorenyl III resulting from C–C coupling. No polymerization occurs at all.



J. Rault-Berthelot (✉) · M.M. Granger
Laboratoire d'Electrochimie Moléculaire et Macromoléculaire,
UMR CNRS No 6510, Université de Rennes I,
Campus de Beaulieu, Avenue du Général Leclerc,
F-35042 Rennes, France
e-mail: joelle.rault@univ-rennes1.fr,
Tel.: +33-2-99286293, Fax: +33-2-99286732

Furthermore, a lot of polynuclear aromatic amines have been studied in the last decades. Some of them are described in Table 1 and may be classified into three main groups: Ar-NH₂, RR'N-Ar-NRR' or Ar¹-NR-Ar². The anodic oxidation of the majority of these

Table 1 Bibliographic summary of various electropolymerized polynuclear aromatic amine compounds

Type	Substituents	Ar	Ref.
ArNH ₂			20, 21
			22
			23–28
			29
			30
R-N-Ar-N-R R'	R=R': H		31–40
			41–44
			45
			41
	R: H and R': C ₂ H ₅		41
	R=R': CH ₃		41
	R: H	Ar ¹ = Ar ² :	46
		Ar ¹ : and Ar ² :	47
		Ar ¹ : and Ar ² :	43
		Ar ¹ : and Ar ² :	48
	Ar ¹ : and Ar ² :	49	
	R: CH ₃ , C ₂ H ₅ , n-Butyl, n-Hexyl Ar ¹ = Ar ² :	50	

compounds leads to the obtainment of more or less homogeneous, smooth and adherent polymer films on the electrode. In each case, the physicochemical properties and the electrochemical behaviour of the polymers are described and a mechanism of polymerization is proposed in the light of the experimental results. Classical polyaniline-type polymerizations are described when the C–N coupling is predominant; in the case of diaminophenylene or naphthalene, ladder polymers may be obtained. Finally, the oxidation product may be a mixture of soluble oligomers from C–C coupling and of insoluble polymers from C–N coupling. In the case of polymers with polyaniline likeness, their study in aqueous medium always shows reversible electroactivity.

We present in this paper the oxidation of **I** in CH₂Cl₂ + 0.2 M Bu₄NBF₄ together with the electrochemical behaviour of the insoluble products obtained on the electrode and studied in organic or aqueous acid medium. Physicochemical features of these compounds are also described.

Experimental

Chemicals

2-Aminofluorene is a commercially available product and was used without additional purification.

Supporting salt

Tetrabutylammonium tetrafluoroborate was obtained from Fluka and recrystallized three times from methanol plus water (1:1) and dried for 48 h under vacuum.

Solvents

Acetonitrile and dichloromethane were obtained from SDS with less than 100 ppm of water (checked by means of the Karl Fischer method) and were used without any purification.

Aluminium oxide

This was obtained from Woelm (Super I), heated at 300 °C under vacuum for 24 h and used at once under argon pressure.

Cells and electrodes

Electrochemical investigations were carried out in three-compartment cells. The anode, cathode and reference electrode were in all cases separated by a glass frit. All potentials refer to the system Ag/(Ag⁺, NO₃⁻), 0.1 M in CH₃CN. For the cyclic voltammetry investigations the working electrode was a 1 mm² stationary platinum disk. For preparative electrolysis the working anode was a rectangular platinum sheet (total area about 9 cm²). In all cases the cathode material was either a vitreous carbon stick or a platinum grill.

All experiments were carried out under an argon atmosphere and, additionally, neutral activated alumina was added to the supporting electrolyte in the working compartment of the cell in order to remove excess moisture.

The three-electrode cells were connected to a PAR Model 173 potentiostat monitored with a PAR Model 175 signal generator and a digital coulometer (PAR Model 179). The cyclic voltammetry traces were recorded on an XY SEFRAM-type TGM 164 recorder.

Polymer analysis

In the course of analysis using cyclic voltammetry the working electrode used was dried in air and used in a second electrolytic solution free of any electroactive species. Contrariwise, after macroelectrolysis the polymer coating the platinum surface was carefully rinsed with the solvent used for the preparative electrolysis, dried in air and then released from the anode. The polymer was rinsed again and dried carefully under vacuum at room temperature for 48 h.

Infrared spectra were recorded using a Fourier transform spectrophotometer (FTIR) from Nicolet (model 205) by diffuse reflectance through the polymer mixed with KBr.

UV-visible spectra were recorded using a Guided Wave model 150 spectrophotometer with optical fibres with a specific arrangement that allowed spectroscopic examination to be performed during an electrochemical reaction. To do this, the polymer was deposited on a concave platinum surface that simultaneously acted as a reflector for the optical beam. The spectroelectrochemical equipment has been described previously [51].

Results and discussion

Cyclic voltammetry analysis

The CVs performed during the anodic oxidation of **I** are greatly dependent on the solvent. Despite the fact that **I** is soluble in CH_2Cl_2 , CH_3CN or their mixture, **I** polymerization occurs only in CH_2Cl_2 . It may be suggested that the charged species (i.e. oligomers) generated in the course of the electropolymerization process would be less soluble in CH_2Cl_2 than in CH_3CN and consequently would precipitate more easily onto the electrode surface. Thus the propagation of the electropolymerization would be facilitated in CH_2Cl_2 .

The oxidation of **I** in the absence of Al_2O_3 (solvent containing small amount of water) leads to the formation on the anodic surface of an insoluble grey-blue deposit. The electrochemical behaviour of this shows an irreversible oxidation and a rapid overoxidation of the matrix leads to a non-electroactive material.

When Al_2O_3 is added to the monomer solution, the **I** oxidation peaks become smaller which seems to indicate some adsorption of **I** on aluminium. However, under these conditions the polymerization occurs. Consequently, owing to the adsorption phenomena, **I** polymerization is better performed in highly concentrated solutions.

Figure 1 A shows cyclic voltammograms recorded during electropolymerization of 2-aminofluorene in $\text{CH}_2\text{Cl}_2 + \text{Bu}_4\text{NBF}_4$ (0.2 M). At the first sweep, two main oxidation peaks are visible at E^1 (0.4 V) and E^2 (1.15 V). Recurrent sweeps up to potentials more anodic than 1.75 V, i.e. much more anodic than E^2 , leads to the polymerization that is visible on the CV by a regular increase of two main waves where threshold potential is about 200 mV less anodic than the E^1 and E^2 ones (Fig. 1B). The electrode is then covered by a yellow deposit. The polymerization occurs better when the oxidation is performed by recurrent cyclic voltametries than when the oxidation is performed at a fixed potential. The nature of the electrode (platinum, graphite or vitreous carbon) does not affect the polymerization process.

Electrochemical behaviour of the polymers

Figure 2 presents the electrochemical behaviour of a deposit formed by CV between -0.4 V and $+1.8$ V (ten sweeps) and studied in CH_2Cl_2 (Fig. 2A), CH_3CN (Fig. 2B) and HCl (Fig. 2C). In each medium the poly-

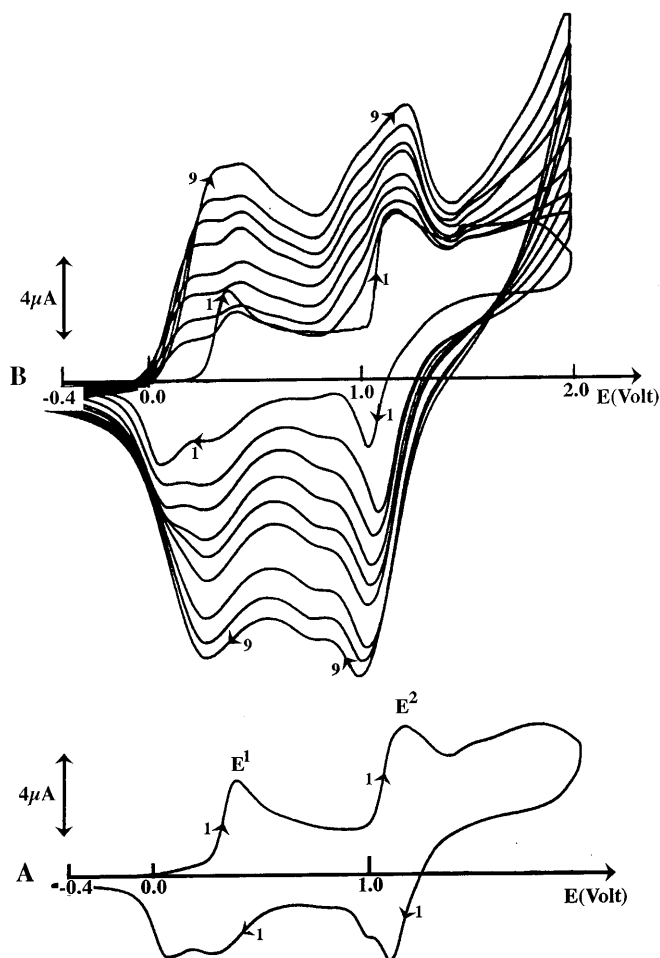
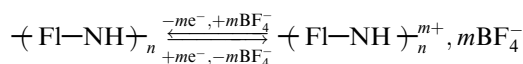


Fig. 1A, B Cyclic voltammograms of a 10^{-2} M solution of 2-aminofluorene in dry $\text{CH}_2\text{Cl}_2 + 0.2$ M Bu_4NBF_4 (containing Al_2O_3). Initial potential: -0.4 V; switching potential: 2.0 V. A one sweep; B nine recurrent sweeps. Scan rate: 100 mV s^{-1} . Working electrode: platinum disk of diameter 1 mm

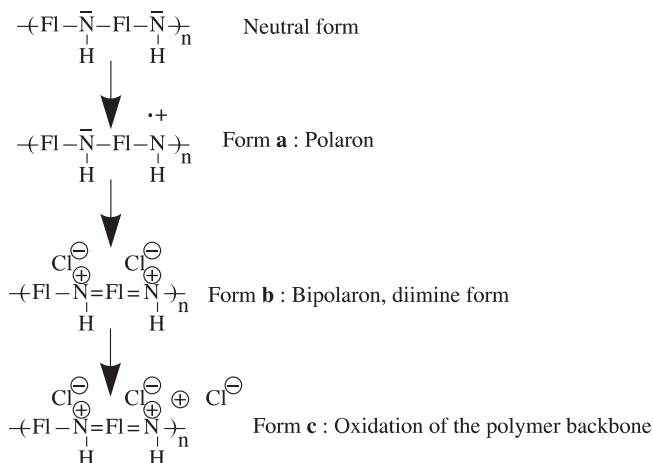
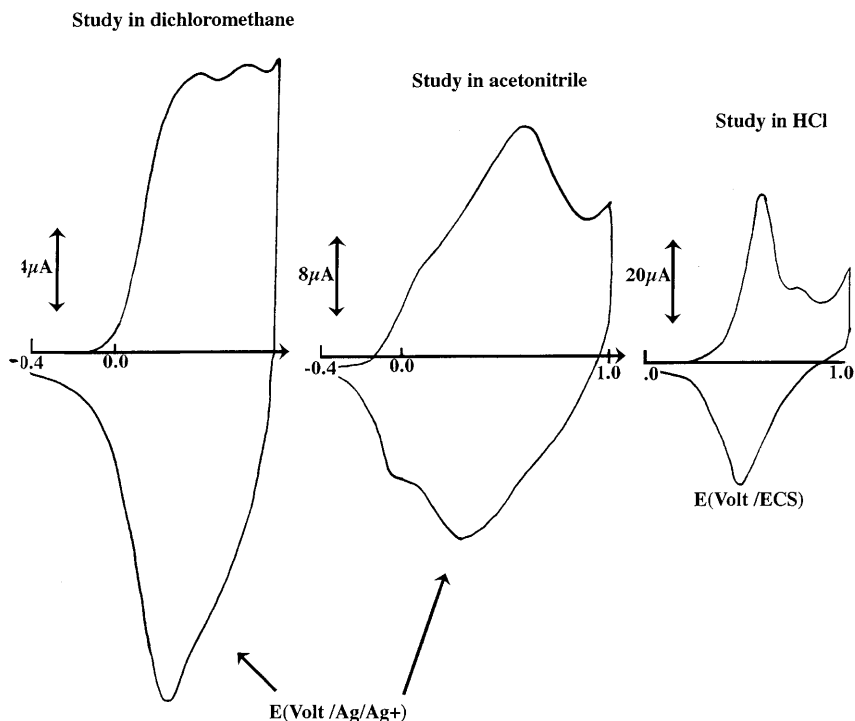
mer presents a reversible and stable p-doping system. In CH_2Cl_2 or in CH_3CN the redox oxidation-reduction process of poly(**I**) corresponds to the equilibrium of Scheme 1.



Scheme 1 Poly(**I**) p-doping process in 0.2 M Bu_4NBF_4 in CH_2Cl_2 or 0.1 M CH_3CN

It must be mentioned that poly(**I**) is the first polyfluorene presenting electroactivity in aqueous medium (Fig. 2C). In such a medium the oxidation leads at first to polarons (Scheme 2, form a) which are oxidized to diimine species of bipolarons (form b); at higher oxidation level the aromatic chain is also oxidized, leading to form c. On the other hand, as is the case for most polyfluorenes in which C-9 is not substituted [52], poly(**I**) does not possess a reversible n-doping system in the cathodic range between -2.0 V and -3.0 V.

Fig. 2A–C Voltametric response at a platinum disk electrode (diameter 1 mm) previously coated with a polymer obtained by ten recurrent sweeps between -0.4 V and $+2.0$ V in a 10^{-2} M solution of 2-aminofluorene in dry CH_2Cl_2 + 0.2 M Bu_4NBF_4 (containing Al_2O_3). Supporting electrolyte: **A** 0.2 M Bu_4NBF_4 in CH_2Cl_2 ; **B** 0.1 M Bu_4NBF_4 in CH_3CN ; **C** 2 N HCl in H_2O . Scan rate: 100 mV s^{-1}

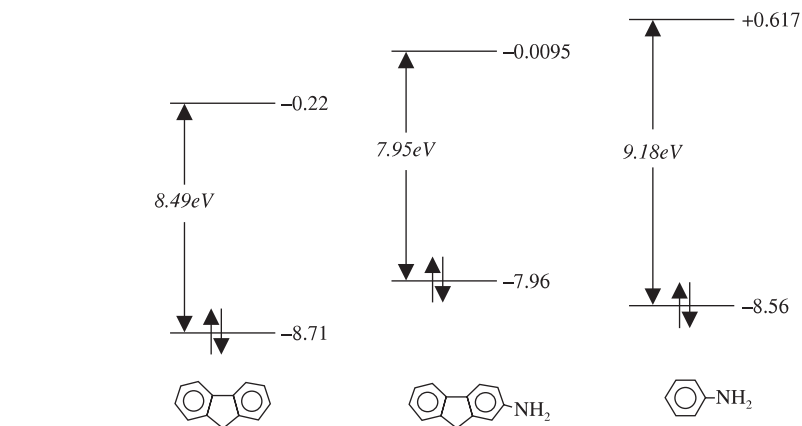


Scheme 2 Poly(I) structure at different oxidation levels in aqueous acid (2 M HCl)

AM1 semi-empirical calculations

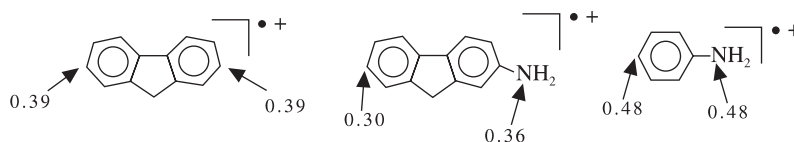
In order to understand better how the polymerization occurs, we performed AM1 semi-empirical calculations [53] using a Mopac program [54] on fluorene, amino-fluorene and aniline. The results are summarized in Scheme 3.

Scheme 4 Atom coefficients in the Singly occupied molecular orbital (SOMO) of the cation radical of the same compounds obtained by AM1 semi-empirical calculations using the MOPAC program



Scheme 3 Values of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels for fluorene, 2-aminofluorene I and aniline obtained by AM1 semi-empirical calculations using the MOPAC program

The value of the highest occupied molecular orbital (HOMO) energy level of fluorene and amino-fluorene are in agreement with the oxidation potential values observed during CV investigations. The mesomeric donor effect of the amino group increases the I HOMO level that renders I more easily oxidizable than fluorene itself.



We then performed AM1 semi-empirical calculations on fluorenes and aniline cation radicals. The results of the atom coefficients in the Singly occupied molecular orbital (SOMO) of each cation radical are reported in Scheme 4. The analysis of the AM1 calculation results shows that in the case of the cation radical of fluorene, aminofluorene and aniline, the highest coefficients in the SOMO are on the atoms expected to be involved in the coupling during a polyaniline-like polymerization. Further theoretical calculations on dimers and trimers of **I** were not possible since these species have too many atoms (our program is limited to calculations on a molecule of 36 atoms).

Physicochemical analysis of the polymers

Infrared spectroscopy

The FTIR absorption spectra in KBr powder of **I** and of poly(**I**) film (oxidized form) were obtained to identify the structure of the polymer. They are presented Fig. 3. In spectrum A, while two peaks corresponding to the NH stretching vibration of the amino groups (labelled **a**) are, as expected, observed at 3360 cm^{-1} and 3445 cm^{-1} , the peak ascribable to the stretching vibration of the CN bonds (labelled **b**) is observed at 1225 cm^{-1} . Characteristic absorption peaks of 2,3-disubstituted and 2,3,5-tri-

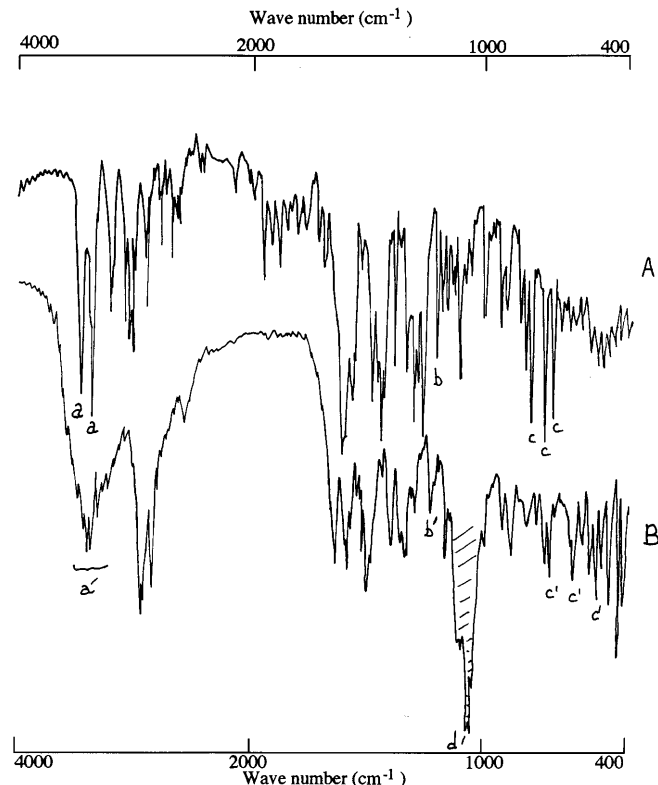


Fig. 3 IR spectra of 2-aminofluorene **A** and of poly(2-aminofluorene) **B** in its p-doped form. **I** as well as poly(**I**) were mixed in KBr and the spectra were obtained by diffuse reflection through the powder using an FTIR spectrophotometer

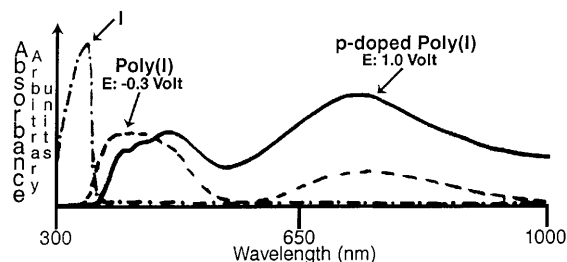


Fig. 4 Visible spectra of 2-aminofluorene (dash-dot line), of neutral poly(**I**) (dashed line) and of p-doped poly(**I**) oxidized at $E = 1.0\text{ V}$ (solid line). The deposits were obtained by anodic oxidation of a 10^{-2} M solution of **I** in $0.2\text{ M Bu}_4\text{NBF}_4$ in CH_2Cl_2 containing Al_2O_3 by 10 recurrent sweeps between -0.4 V and $+2.0\text{ V}$. Area of the platinum electrode: 20 mm^2

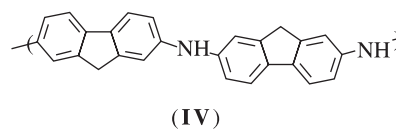
substituted which arise from the in-plane and out-of-plane CH bending modes (labelled **c**) were observed in the range $750\text{--}850\text{ cm}^{-1}$. As generally observed, the poly(**I**) spectrum presents broader vibration bands. However, most of the bands observed in the monomer spectrum are observed in the polymer spectrum. The two bands **a** are transformed to a large band **a'**. The band **d'** corresponds to the vibration bands of the dopant anion BF_4^- . A modification is observed for the in-plane and out-of-plane CH bending modes owing to the transformation of the 2,3-disubstituted benzene rings into a 2,3,5-trisubstituted one (bands **c'** between 600 nm and 750 nm).

UV-visible spectra

Figure 4 shows the UV-visible spectrum of **I** as a single wave with a maximum at 350 nm . The spectra of an as-obtained poly(**I**) and of a p-doped poly(**I**) polarized at 1.0 V in Bu_4NBF_4 (0.1 M) in CH_3CN are also shown. They present two waves with maxima at 420 nm and 730 nm . The second wave corresponding to the conduction band increases with the doping level as expected.

Conclusion

We conclude that films of poly(**I**) could be prepared by repeated cycling in CH_2Cl_2 containing $0.2\text{ M Bu}_4\text{NBF}_4$. The films prepared show electroactivity both in organic solvents and in acidic water; their electrochemical behaviour resembles that of polyaniline synthesized in the same medium. On the basis of the IR absorption spectral data, AM1 semi-empirical calculations, the electrochemical characterization of the poly(**I**) and previous results concerning the electropolymerization of other NH_2 group-containing aromatic compounds, the structure **IV** for poly(**I**) may be proposed.



Acknowledgements The authors wish to thank UMR CNRS 6510 for financial support.

References

- Rault-Berthelot J (1998) *Recent Res. Devel. In Macromol. Res.*, 3
- Rault-Berthelot J, Simonet J (1985) *J Electroanal Chem* 182: 187
- Rault-Berthelot J, Angely L, Delaunay J, Simonet J (1987) *New J Chem* 11: 487
- Rault-Berthelot J, Simonet J (1986) *New J Chem* 10: 169
- Rault-Berthelot J, Mabon G, Simonet J (1988) *J Electroanal Chem* 240: 355
- Rault-Berthelot J, Orliac MA, Simonet J (1988) *Electrochim Acta* 33: 811
- Simonet J, Rault-Berthelot J, Granger MM, Le Deit H (1994) *J Electroanal Chem* 372: 185
- Rault-Berthelot J, Granger MM (1996) *Synth Met* 82: 103
- Rault-Berthelot J, Massaoudi M, Rozé C (1995) *J Electroanal Chem* 388: 187
- Rault-Berthelot J, Massaoudi M, Le Deit H, Simonet J (1995) *Synth Met* 75: 11
- Rault-Berthelot J, Granger MM (1993) *J Electroanal Chem* 353: 341
- Rault-Berthelot J, LeDeit H, Massaoudi M, Simonet J (1995) *J Electroanal Chem* 380: 237
- Rault-Berthelot J, Rozé C, Granger MM (1997) *J Electroanal Chem* 436: 85
- Rault-Berthelot J, Rozé C (1998) *Synth Met* 93: 97
- Rault-Berthelot J, Rozé C (1997) *J Electroanal Chem* 435: 157
- Rault-Berthelot J, Cariou M, Tahri-Hassani J (1996) *J Electroanal Chem* 402: 203
- Rault-Berthelot J, Rozé C, Granger MM, Raoult E (1999) *J Electroanal Chem* (in press)
- Yasukouchi K, Taniguchi I, Yamaguchi H, Miyaguchi K, Horie K (1979) *Bull Chem Soc Jpn* 52: 3208
- Waltman RJ, Bargon J (1985) *J Electroanal Chem* 194: 49
- Genies EM, Penneau JF, Lapkowski M (1988) *New J Chem* 12: 765
- Kobayashi N, Yamada K, Hirohashi R (1992) *Electrochim Acta* 37: 2101
- Guay J, Leclerc M, Dao LH (1988) *J Electroanal Chem* 251: 31
- Vettorazzi N, Silber JJ, Sereno L (1981) *J Electroanal Chem* 125: 459
- Vettorazzi N, Silber JJ, Sereno L (1983) *J Electroanal Chem* 158: 89
- Marioli JM, Silber JJ, Sereno L (1989) *Electrochim Acta* 34: 127
- Arevalo AH, Fernandez H, Silber JJ, Sereno L (1990) *Electrochim Acta* 35: 741
- Lacroix JC, Mostefai M, Havard G, Pham MC, Doucet JP, Lacaze PC (1995) *New J Chem* 19: 979
- Ohsaka T, Kunimura S, Oyama N (1988) *Electrochim Acta* 33: 639
- El-Rahman HAA, Schultze JW (1996) *J Electroanal Chem* 416: 67
- El-Rahman HAA, Ohsaka T, Kitamura F, Tokuda K (1991) *J Electroanal Chem* 315: 161
- Ekinci E, Karagözler AA, Karagözler AE (1996) *Synth Met* 79: 57
- Maihle-Randolph C, Desilvestro J (1989) *J Electroanal Chem* 262: 289
- Mailhé-Randolph C, McEvoy AJ (1989) *Ber Bunsenges Phys Chem* 93: 905
- Si SH, Xu YJ, Nie LH, Yao SZ (1995) *Electrochim Acta* 40: 2715
- Davis J, Vaughan DH, Cardosi MF (1996) *Electrochim Acta* 41: 2375
- Chiba K, Ohsaka T, Oyama N (1987) *J Electroanal Chem* 217: 239
- Levi MD, Pisarevskaya EY (1992) *Electrochim Acta* 37: 635
- Kitani A, Yano J, Sasaki K (1986) *J Electroanal Chem* 209: 227
- Chiba K, Ohsaka T, Ohnuki Y, Oyama N (1987) *J Electroanal Chem* 219: 117
- Malitesta C, Palmisano F, Torsi L, Zamboni PG (1990) *Anal Chem* 62: 2735
- Azzem MA, Yousef US, Limosin D, Pierre G (1996) *J Electroanal Chem* 417: 163
- Jackowska K, Bukowska J, Jamkowski M (1995) *J Electroanal Chem* 388: 101
- Lee JW, Park DS, Shim YB, Park SM (1992) *J Electrochem Soc* 139: 3507
- Oyama N, Sato M, Ohsaka T (1989) *Synth Met* 29: E501
- Chandrasekhar P, Gumbs RW (1991) *J Electrochem Soc* 138: 1337
- Hayat U, Bartlett PN, Dodd GH (1987) *J Electroanal Chem* 220: 287
- Nguyen MT, Dao LH (1990) *J Electroanal Chem* 289: 37
- Dong S, Li Z (1990) *Synth Met* 38: 381
- Kitani A, Yano J, Kunai A, Sasaki K (1987) *J Electroanal Chem* 221: 69
- Nguyễn MT, Dao LH (1990) *J Chem Soc Chem Commun* 1221
- Rault-Berthelot J, Questaigne V, Simonet J, Peslerbe G (1989) *New J Chem* 13: 45
- Rault-Berthelot J, Angely L, Delaunay J, Simonet J (1987) *New J Chem* 11: 487
- Dewar MJS, Zoebish EG, Healy EF, Stewart JJP (1985) *J Am Chem Soc* 107: 3902
- Stewart JJP MOPAC version 6.0, QCPE 504 on PC, USAF Academy