

New polyfluorenylidenes substituted by donor or acceptor groups

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RÉSUMÉ

L'oxydation anodique des fluorénylidènes **I**, **II** et **III** conduit dans des conditions expérimentales définies à des polymères dont l'état d'oxydation varie avec le potentiel auquel ils sont polarisés. La présence de groupement(s) cyano dans les poly(**II**) et (**III**) permet la préparation de composites polymère-métal (Au, Ag, Pt, Pd). Ces composites ont été utilisés comme matériau d'électrode lors de l'oxydation de différents substrats (hydrazine, méthanol, formaldéhyde, azoture ...)

Mots-clés : oxydation anodique, électropolymérisation, composite polymère-métal, polymère conducteur, fluorénylidène.

ABSTRACT

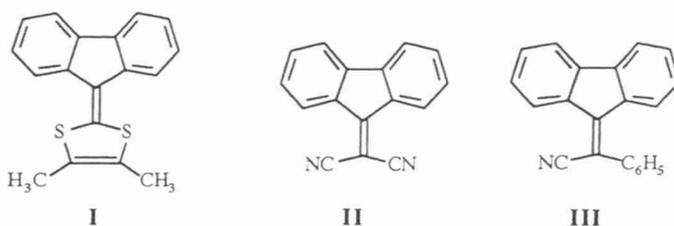
The anodic oxidation of fluorenylidenes **I**, **II** or **III** leads in specific experimental conditions to polymers. The presence of cyano group(s) in poly(**II**) and (**III**) allows the formation of polymer-metal composites (Au, Ag, Pt, Pd). These composites are used as electrode material during the oxidation of various substrates (hydrazine, methanol, formaldehyde, azides...)

Key words : anodic oxidation, electropolymerization, polymer-metal composite, conducting polymer, fluorenylidene.

INTRODUCTION

Since the synthesis of the first polyfluorene in 1985 (1), many 9-mono- and 9,9-disubstituted polyfluorenes were prepared and studied (2). We report here, the anodic polymerization of three new methylenefluorenes, one substituted by a donor group : 2-(9H-fluoren-9-ylidene)-4,5-dimethyl-1,3-dithiole (**I**) and two others by attracting

cyano group(s): 2-(9*H*-fluoren-9-yliden)-malononitrile (**II**) and 2-(9*H*-fluoren-9-yliden)-2-phenylacetonitrile (**III**).



EXPERIMENTAL

Monomers synthesis and electrochemical settings are described elsewhere (3-5).

RESULTS

Polymerization

Cyclic voltammetry investigation

Figure 1 reports the cyclic voltammograms of each monomer in dry and deaerated $\text{CH}_2\text{Cl}_2 + 0.2\text{M Bu}_4\text{NBF}_4$ solutions. **I** is oxidized at very low anodic potential ($E^1 = 0.46\text{V}$) and **II** at very high anodic potential ($E^1 = 1.85\text{V}$), **III**'s oxidation is between. The electronic impoverishment of the double bond by the cyano group(s) renders **II** and **III** less easily oxidizable than **I** which double bond undergoes the donor effect of the dithiole group.

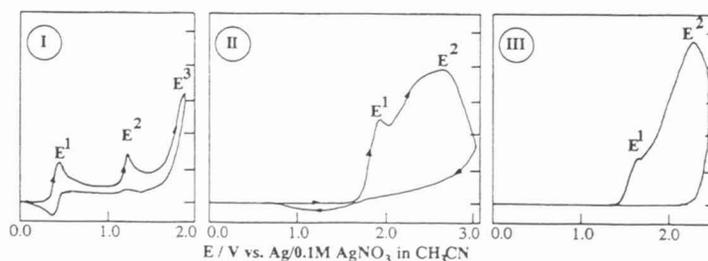


Figure 1 : Cyclic voltammogram recorded at a platinum electrode (diameter 1 mm) of a 10^{-2}M **I**, **II** and **III** solutions in $\text{CH}_2\text{Cl}_2 + 0.2\text{M Bu}_4\text{NBF}_4$. Sweep rate: $100\text{mV}\cdot\text{s}^{-1}$.

Polymerization at fixed potential

Chronoamperometric measurements determined the best polymerization potential of each compound (1,85V for **I** and **II**; 1,7V for **III**). After consumption of a sufficient amount of electricity, the anode is covered by deposits which physicochemical properties have been studied (3,5).

Polymers electrochemical behaviour

Anodic behaviour

The anodic response of each polymer consists in a reversible p-doping process which threshold potential is in accordance with the substituent effect of each fluorenylidene methylene bond. Poly(I) is more easily p-doped than poly(II) and poly(III).

Cathodic behavior of each polymers

Figure 2 reports the cathodic response of each polymer. Poly(I) is reduced at potential more cathodic than $-2,0\text{V}$, the reduction process is irreversible and leads to a main modification of the further anodic behaviour (labelled 2 to n). Reduction of poly(II) occurs since -250mV . A stable and reversible cathodic signal is observed between $0,0$ and $-1,4\text{V}$. Finally, poly(III) is reduced in between and a stable and reversible redox system is observable between $-1,0$ and $-2,0\text{V}$.

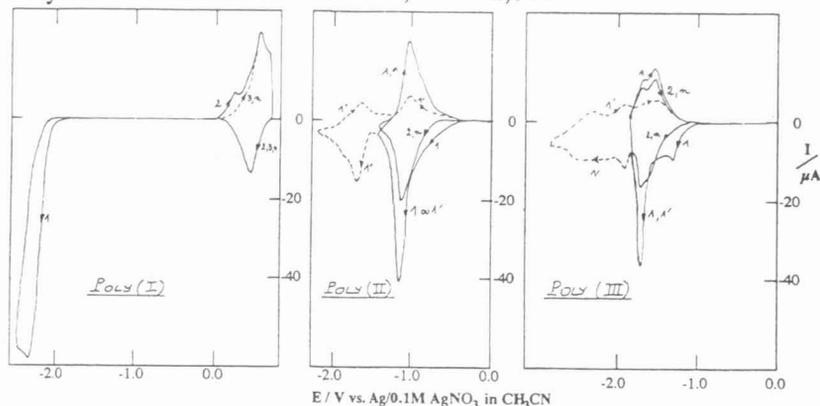


Figure 2 : Cyclic voltammograms at platinum-poly(I, II and III) electrode obtained by anodic oxidation of $5 \cdot 10^{-3}\text{M}$ solution of I, II and III in $\text{CH}_2\text{Cl}_2 + 0,2\text{M Bu}_4\text{NBF}_4$ at fixed potential. The study is performed in $\text{CH}_3\text{CN} + 0,1\text{M Bu}_4\text{NBF}_4$. Sweep rate: $100\text{mV}\cdot\text{s}^{-1}$.

The values of the threshold potential are in accordance with the donor or acceptor effect of the fluorenylidene methylene substituent. Further reduction of the poly(II) and (III) may be performed at more negative potential but their reversibility is not so good and leads to a partial over-reduction of the polymer matrix. An n-doping process of the poly(III) is observable between $-2,0$ and $-2,8\text{V}$. This n-doping confers to the poly(III) catalytic properties when it is used as electrode modifier during the cathodic reduction of activated compounds (reduction potential of the (\pm) -*trans*-1,2-dibromocyclohexane: $-3,0\text{V}$ on platinum, $-2,1\text{V}$ on poly(III)).

Microcoulometries performed on each polymer explain the mechanism of polymerization of each polymer as well as their electrochemical behaviours. The three poly-

mers are obtained under their dicationic p-doped level. The reduction at 0,0V leads to the partial reduction of the materials under their cationic forms. The total reduction of the polymer matrix occurs then during the cathodic treatment at highly negative potential for the poly(I) and at less and less negative potential for the poly(III) and (II). Each polymer may then be reoxidized at their E^1 and E^2 potentials during further anodic investigations. These new materials may then exist under their p-doped dicationic, cationic, neutral, anionic, dianionic or n-doped dianionic forms depending on the polymer and its polarization potential.

Formation and use of poly(II) and poly(III)-metal composites

Formation of polymer-metal composites

The presence of the cyano group(s) in the poly(II) and poly(III) skeleton leads us to test the affinity of these interfaces towards metallic cations. Since the polymer are obtained, after reduction at 0.0V, under their cationic forms, a previous reduction of the polymer matrix is performed at respectively -1.7V and -1.8V. The reduced polymer is then soaked in a solution of the metallic cation during 30mn. After activation of the metal by reduction up to its zero state, the polymer-metal composite are studied in aqueous acid solutions. The affinity of gold, silver, palladium and platinum towards poly(II) and poly(III) has been demonstrated since the polymer-metal composites possess the same electrochemical behaviour as pure metal electrodes studied in same conditions.

Use of the polymer-metal composites

The polymer-metal composites are used as electrode material for the detection of glucose, hydrazine, sodium azide, methanol,... in aqueous media (5). As an example catalytic oxidation waves are obtained mainly with gold and palladium : at 0,8V/SCE for hydrazine and at 0,3V/SCE for methanol. Moreover the best detection limit of NaN_3 never published is obtained with poly(II+Au) in pH7,3 : $2,5 \cdot 10^{-5}\text{M}$

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