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Synthesis and Electrochemical Behaviour of Some Polymers Issued From Halogenated Derivatives of Pyrrole

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SYNTHESIS AND ELECTROCHEMICAL BEHAVIOUR OF SOME POLYMERS
ISSUED FROM HALOGENATED DERIVATIVES OF PYRROLE

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Abstract β -Halogenated pyrroles, like pyrrole itself, give by electrochemical oxidation polymers with conductivities ranging in the field 10^{-5} - 10^{-2} $\Omega^{-1} \times \text{cm}^{-1}$. Polymers issued from 3,4-diiodo, 3,4-dibromo, 3,4-dichloro, and 3-bromo pyrroles have been examined and form stable, reproducible redox systems when deposited on a Pt disk electrode. 3,4-diiodopyrrole particularly shows well behaved peaks. All polymers can be reduced, leaving back 15% to 20% of the quantity of coulombs necessary to their synthesis. Some bromopyrroles own the property to autopolymerize when handled in concentrated solutions, with evolvment of bromhydric acid. These polymers have a relatively good conductivity (10^{-2} - $10 \Omega^{-1} \times \text{cm}^{-1}$), and constitute easy to obtain study materials.

INTRODUCTION

In order to understand better the relations between structure and substitution in pyrrole polymers, the compared behaviour of four halopyrroles has been examined. At the same time, it was found that some bromopyrroles owned the property to decompose spontaneously into conducting polymers. It is of our interest to show the preliminary results on these "autopolymers" in this communication. All the potential values given in this paper are determined v s. $\text{Ag}/10^{-2} \text{ M Ag}^+$.

POLYMERS ISSUED FROM ELECTROCHEMICAL OXIDATION OF HALOPYRROLES

3,4-diiodo, 3,4-dibromo, 3,4-dichloro and 3-bromo pyrroles^{1,a,b}

can be electropolymerised on a platinum electrode. Films of polymer furnish stable electrochemical systems, with well behaved peaks at higher potentials than polypyrrole ⁽²⁾ (Fig. 1). Peak potentials of the monomers and the polymers were correlated with the substituent electronegativity (Fig. 2), showing a strong inductive effect of the halogen.

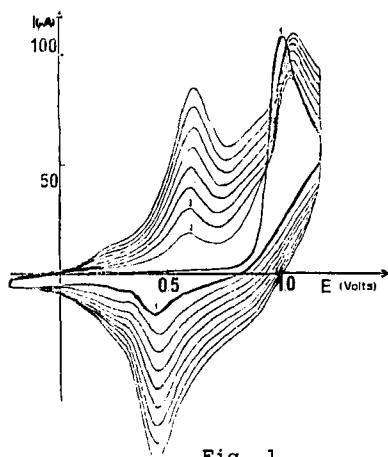


Fig. 1

Cyclic voltammetry of
3,4-diiodopyrrole ; $v = 100$ mV/s
Electrolyte : $\text{CH}_3\text{CN}/\text{LiClO}_4$, 0,1 M

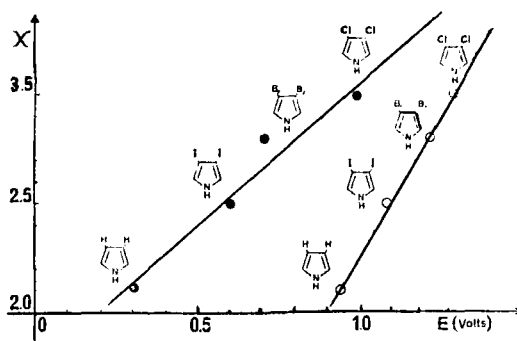






Fig. 2

Correlation between the peak
potentials and the substituent
electronegativity (Pauling)

Films of polymer generally adhere to the electrode and have to be scraped in fine powders and pressed in pellets to perform conductivity measurements. The low values obtained with all the samples are probably due mainly to sterical crowding disrupting the planarity of the chains. However, the greater electron-withdrawing power of chlorine is probably responsible for the difference in conductivity, anomalous versus steric factors, observed between 3,4-dibromo and 3,4-dichloro pyrroles. and E_p values are summarized in the following table.

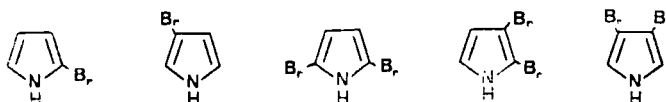
Peak potentials and conductivities of polyhalopyrroles

				
E_p^m (V)	1.07	1.07	1.22	1.27
E_p^p (V)	around 0.3	0.60	0.70	0.97
σ ($\Omega^{-1}\text{cm}^{-1}$)	3×10^{-2}	9×10^{-4}	8×10^{-3}	2×10^{-4}

E_p : Peak potential $\left\{ \begin{array}{l} m: \text{monomer} \\ p: \text{polymer} \end{array} \right.$ σ : Conductivity

AUTOPOLYMERS ISSUED FROM BROMOPYRROLES

The five following compounds are only stable in diluted solutions



Upon removal of solvent, each compound reacts rapidly on itself to give a black, conducting polymer with evolution of bromhydric acid. The reaction is carried out under argon and microanalytical analyses show that the pyrrole moiety is retained inside the material, with a variable amount of bromine according to the compound. Conductivities are rather good and rank from 10^{-3} to $10 \Omega^{-1}\text{cm}^{-1}$. By mixing the polymer with furnace black (1/1) and a drop of electrolyte, a conductive paste is obtained which can be electrochemically cycled with the help of the electrode shown on Fig. 3. The autopolymer of 3-bromopyrrole, chosen as a test compound, neatly presents a stable redox couple at a potential close to polypyrrole potential. The first cycle in reduction is sharper and slightly shifted toward negative potentials (Fig. 4). Another couple (not shown on the figure), which may be attributed to bromine ions inside the material, appears at +0,3V but complete cycling leads to rapid material degradation. All peak flattened then after three cycles.

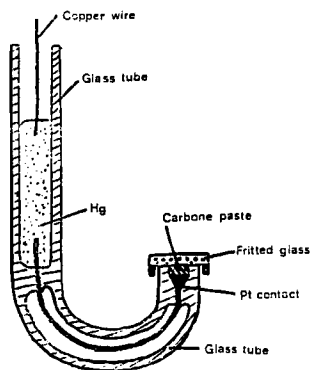


Fig. 3

Carbene paste electrode

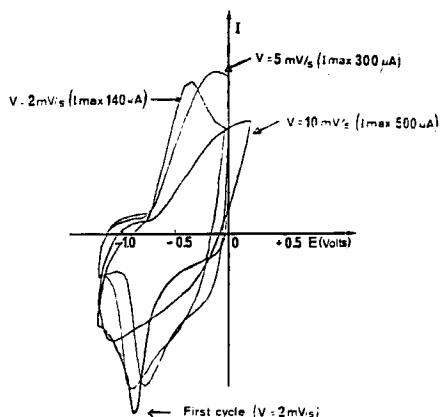


Fig. 4

Cyclic voltammogram of the
autopolymer issued from3-bromopyrrole in $\text{CH}_3\text{CN}/\text{LiClO}_4$ 0.1M

In addition, the dependance in temperature of the conductivity follows the "variable range hopping" law (3), and solid ^{13}C N.M.R. spectrum of the autopolymer is identical (to the experimental differences) to the one obtained with classical electrochemical polypyrrole BF_4^- (4).

CONCLUSION

Stable substituted polymers can be obtained from halogenated derivatives of pyrrole, however they are generally poorly conductive and therefore less ordered than simple polypyrrole (5). They behave then differently than poly(3-methylpyrrole) and poly(3,4-dimethylpyrrole) (6). The comparison of these derivatives with polypyrrole and some thiophenic analogues (7,8) should help to understand the structure-properties relationships in polyheterocycles.

On the other hand, the first results on the autopolymers give some presumption that they are in fact closely apparented to bromine doped polypyrroles. Because of their synthesis without external agent, they could so extend the field of applications for polypyrrole. Further studies are trying to confirm this view.

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