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INFLUENCE OF 3-4 SUBSTITUTIONS ON PROPERTIES OF FIVE MEMBERED POLYHETEROCYCLES

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Abstract : Thin films of 3-4 substituted 5-membered polyheterocycles derived from pyrrole and thiophene have been electrochemically synthesized, showing reversible electrochemical oxidation and reduction processes, and conductivities varying between 10^{-4} and $10^2 \Omega^{-1} \cdot \text{cm}^{-1}$. The absorption spectra of their doped and undoped states, their switching time and lifetime make some of these polymers interesting for electrochromic applications.




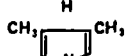





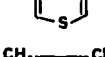


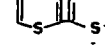

INTRODUCTION

Five membered heterocycles as pyrrole ¹, thiophene, furan ² have been shown to polymerize by α - α' coupling in an electrolytic medium, leading to doped conducting polymers. The high rate of the electrochemical doping-undoping process, with a change of the absorption spectrum make them attractive as electrochromic compounds ³. In this regard, the position 3 and 4 appear interesting for the analysis of the substituent effect on electrospectrochemical properties.

SYNTHESIS AND PROPERTIES OF POLYMERS

These polymers have been electrochemically generated in CH_3CN , 0.1 M monomer and 0.5 M supporting salt. The films were grafted on rough and polished Pt electrodes. The oxidation potential varied with the monomer (Table I) in agreement with the electronic effect of the heteroatom and of the substituents. The conductivities vary in a large range, revealing varying degrees of the stereoregularity of the polymer.

TABLE I - DATA OF IN CH₃CN POLYMERIZED HETEROCYCLES
(1) Current density 150uA / cm² - Electrolyte salt Et₄NBF₄
(2) Non uniform films (3) Thin films (4) Pressed pellets

MONOMER	OXYDATION POTENTIAL OF MONOMER V vs SCE	POLYMER			
		GROWTH RATE Å/min (1)	OXYDATION POTENTIAL V vs SCE	REDUCTION POTENTIAL V vs SCE	CONDUCTI - VITY Ω ⁻¹ cm ⁻¹
	0.8	210	-0.12	-0.29	10 ² (3)
	0.8	250	0.44	0.39	10 ⁻⁴ (3)
	0.75	150	0.15	0	—
	0.35	(2)	0.1	-0.1	0.2(3)
	0.65	(2)	0.23	0.06	10 ⁻⁴ (4)
	1.13	350	0.9	0.75	—
	1.2	350	0.9	0.75	10 ⁻³ (3)
	1.6	100	1.12	0.75	10 (3-4)
	1.4	100	0.9	0.4	10 ² (4)
	1.35	—	1.1	0.77	50 (4)
	1.1	250	1.30	1.0	—
	1.1	250	1.02	0.6	10 ⁻⁴ (3)
	1.3	500	1.25	0.7	4 10 ⁻⁴ (4)
	0.88	500	0.95	0.85	10 ⁻⁵ (3)

An interesting case is given by polythiophene and poly 2,2'bithiophene, which show a conductivity ratio of 10^5 , although a same polymer could have been expected. The polymer films, exhibit reversible cyclic voltammograms (fig.1). The amount of charge involved in the oxidation and in the reduction processes is almost equal, and is about 1/10 of the charge needed for the polymerization. The anodic and cathodic peak currents are proportional to the scan rate, characteristic of an electroactive film on an electrode where diffusion phenomena do not exist. In almost all cases, the reduction wave appears broader, as observed for polythiophene and polypyrrole.

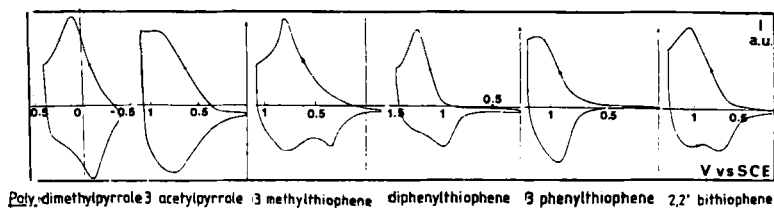


FIGURE 1 Cyclic voltammograms (Electrolyte : $\text{Et}_4\text{BF}_4/\text{CH}_3\text{CN}$)

The absorption spectra of the undoped forms (fig.2) agree with long conjugated chains, polythiophene derivatives appearing red ($\lambda_{\text{max}} \approx 480 \text{ nm}$) and polypyrrole derivatives appearing yellow ($\lambda_{\text{max}} \approx 420 \text{ nm}$). The corresponding doped states absorb uniformly with a very broad band from 600 to 3000 nm. This band is related to the presence of free carriers.

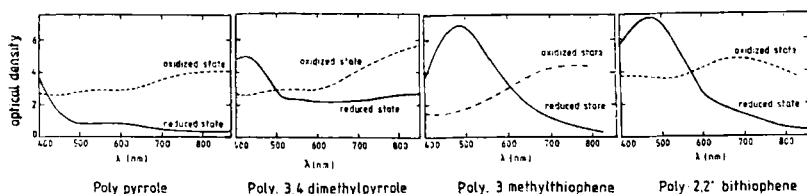




FIGURE 2






Table II lists the different colours and electrooptical efficiencies that can be obtained when cycling various polymers within a determined potential range.

TABLE II (Electrolyte : $\text{Et}_4\text{N BF}_4$)

X		R_2	colour		Potential range (V vs SCE)	ΔOD (mC.cm^{-2})
			oxidized	reduced		
NH	H	H	brown	yellow	0 - + 0.7	0.1 (500nm)
NH	H	COCH_3	yellow-brown	brown-yellow	0 - + 1.1	0.1 (580nm)
NH	CH_3	CH_3	purple	green	-0.5 - + 0.5	0.05 (440n)
NCH_3	H	H	brown-red	orange-yellow	0 - + 0.8	0.05 (500nm)
S	H	CH_3	blue	red	0 - + 1.1	-
S	CH_3	CH_3	deep-blue	blue	+ 0.5 - + 1.5	-
S	H	ϕ	green-blue	yellow	0 - + 1.5	-
S	ϕ	ϕ	blue-gray	yellow	+ 0.5 - + 1.5	-
			blue-gray	red	0 - + 1.3	0.05 (480nm)

The switching time (Table III) appeared to be dependant on the state of the electrode. On rough Pt, the observed switching time was much longer than on polished Pt, as if a resistance effect took place, which could be attributed to an inhomogeneous grafting of the polymer. This might be due to field inhomogeneities on this type of electrode during the polymerization. The switching times obtained on polished Pt appear very interesting for an electrochromic effect. The life times determined in rough conditions, under uncontrolled atmosphere are promising for some polymers (up to 10^5 cycles).

TABLE III

MONOMER	ANION	SWITCHING TIME (ms)			LIFE TIME (cycles)
		Rough Pt Electrode		Polished Pt	
		τ_{ox}	τ_{red}	τ_{red}	
	BF_4^- ClO_4^-	110 140	80 100	20	$\left\{ 2 \cdot 10^4 \text{ (rough Pt)} \right.$
CH_3  CH_3	BF_4^-	450	250	-	-
	BF_4^- Cl_4^-	150	100	-	-
	BF_4^- Cl_4^-				
	BF_4^- Cl_4^-	120 -	90 -	$\left\{ 12 \right.$	$\left\{ \begin{array}{l} > 10^4 \text{ (rough Pt)} \\ > 10^4 \text{ (polished Pt)} \end{array} \right.$

In conclusion, high contrast between the colours of the two states low addressing voltages, as well as improvements concerning switching time and life time make some of these 5 membered polyheterocycles attractive candidates for electrochromic display devices.

REFERENCES

1. A.F. Diaz, K.K. Kanazawa and G.P. Gardini
J.Chem. Soc. Chem. Comm. 637 (1979)
2. G. Tourillon and F. Garnier
J. Electroanal. Chem., 135, 173 (1982)
3. M. Gazard, J.C. Dubois, M. Champagne, F. Garnier, G. Tourillon
J. Phys. C3-537 (1983)