

Poly-N-Methylpyrrole: Kinetic Study.

A. Cambra, M.I. Redondo and M.J. González-Tejera
Dpto. Química-Física I, Facultad de CC. Químicas,
Universidad Complutense de Madrid, Avda.
Complutense s/n, 28040 Madrid (Spain)

The kinetic polymerization study of poly-N-Methylpyrrole doped with perchlorate anions (PNMPy/ ClO_4^-) was performed from three types of techniques: a) Microgravimetric b) Chronoamperometric and c) Cyclic voltammetry.

PNMPy/ ClO_4^- was obtained potentiostatically at $\eta_p=0,5$ V vs Ag/Ag⁺ in non-aqueous medium of MeCN.

Taking into account that the polymerization rate, R_p ($\text{mg cm}^{-2} \text{s}^{-1}$), depends on both monomer and electrolyte (E) concentration:

$$R_p = k [E]^a [M]^b \quad (1)$$

The values of reaction order can be calculated by analysing the effect of monomer concentration on R_p at

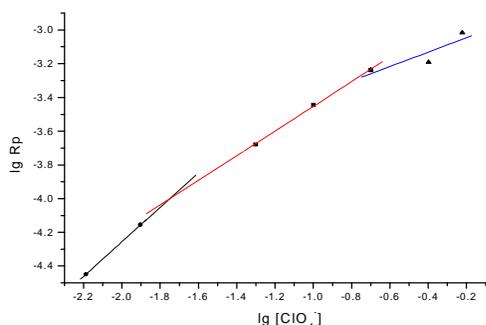


Figure 1. Logarithmic plot of electropolymerization rate vs electrolyte concentration.

- $[\text{ClO}_4^-] = 6,5 \cdot 10^{-3} \text{ M}$ y $1,25 \cdot 10^{-2} \text{ M}$ — Slope = 1,0
- $[\text{ClO}_4^-] = 5 \cdot 10^{-2} \text{ M}$, 0,1 M y 0,2 M — Slope = 0,73 \pm 0,02
- ▲ $[\text{ClO}_4^-] = 0,2 \text{ M}$, 0,4 M y 0,6 M — Slope = 0,4 M \pm 0,2

constant electrolyte concentration and inversely.

a) From the microgravimetric data the weight of the polymer generated was evaluated versus the polymerization time for seven concentration values of the dopant anions ($6,5 \cdot 10^{-3}$, $12,5 \cdot 10^{-3}$, $5 \cdot 10^{-2}$, $1 \cdot 10^{-1}$, $2 \cdot 10^{-1}$, $4 \cdot 10^{-1}$ and $6 \cdot 10^{-1}$ M) maintaining the monomer concentration constant (0,1 M). The slopes of these linear relationships are the polymerization rate, R_p per unit area and time and can be expressed in an exponentially or logarithmically way, Figure 1 and eqs (2) and (3), respectively¹:

$$R_p = k' [E]^a \quad (2)$$

$$\text{Log } R_p = \text{log } k' + a \text{ log } [E] \quad (3)$$

The double logarithmic plot of the R_p against the electrolyte concentration yields a straight line, from whose slope the order of the electrolyte reaction can be calculated.

In this work depending on the electrolyte concentrations range, three slopes values were found, see Figure 1.

In a similar way, the monomer concentration was varied ($5 \cdot 10^{-2}$, $1 \cdot 10^{-1}$, $3 \cdot 10^{-1}$, $5 \cdot 10^{-1}$, $6,5 \cdot 10^{-1}$ and $8 \cdot 10^{-1}$ M) and the electrolyte one remained constant (0,05 M). With similar plots that in the former case the order of reaction of the monomer reaction can be determined, eqs (4) and (5):

$$R_p = k'' [M]^b \quad (4)$$

$$\text{Log } R_p = \text{log } k'' + b \text{ log } [M] \quad (5)$$

From Figure 2 the reactions order was 0,54.

b) Assuming that the polymerization charge density was proportional to the electrogenerated polymer weight being constant the relationship $W_{\text{polymer}}/W_{\text{electrolyte}}$, the next equation can be established:

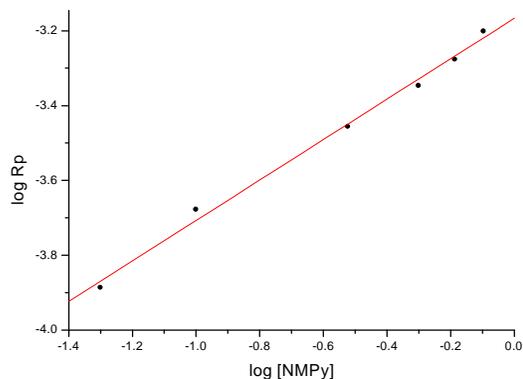


Figure 2. Logarithmic plot of electropolymerization rate vs monomer concentration. — Slope 0,54 \pm 0,02.

$Q_p = k''' M$ where k''' is the charge density per milligram of generated polymer, that is the charge productivity.

Therefore: $dQ_{\text{pol}}/dt = k''' dM/dt = k''' R_p$ (6) and

$\text{Log } dQ_p/dt = \text{log } k''' + \text{log } k + a \text{ log } [E] + b \text{ log } [M]$ (7)

Reactions orders can be obtained from Q_p at different polarization times from solutions with different monomer or electrolyte concentrations.

c) The storage efficiency, Q_{ox}/W (mC mg^{-1}) can be deduced from the characterization voltammograms and has to be proportional to the weight of the electrogenerated polymer². Similarly at the a) and b) cases is possible to establish a logarithmic relationship between the storage efficiency and the monomer or electrolyte concentration and to obtain the two reaction orders.

- 1- T.F. Otero, E. Angulo, *Journal of Applied Electrochemistry* 22 (1992) 369-375.
- 2- I. Villarreal, E. Morales, J.L. Acosta, *Polymer Physics*, Vol. 38, 1258-1266 (2000).