

A NEW POLYMERIC BLEND POLYPYRROLE-POLY(MALEIC ACID-CO-OLEFIN). ELECTROGENERATION, PRODUCTIVITIES AND SPECIFIC CHARGES

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ABSTRACT

The influences of the polymerisation condition on both, production and properties of electrochemically synthesised polypyrrole film in presence of poly(maleic acid-co-olefin) were studied. Polymerisation variables as polymerisation potentials, polarisation times, concentration of pyrrole and concentration of poly(maleic acid-co-olefin) were followed by their influence on both, productivity of the polymerisation charge and the ability to store charge in every electrogenerated film.

Keywords: polypyrrole, poly(maleic acid-co-olefin), composite, synthesis

INTRODUCTION

Conducting polymers, having new and interesting properties, were developed by generation of polymeric blends. By incorporation of molecules possessing desired properties like the type of charge, electroactivity, size and geometrical structure, complexation, acido-basicity, etc. [1,2]. A method to immobilise functional molecules in conducting polymers is by compensation of charge during electropolymerisation. During the electrochemical polymerisation, a stoichiometric amount of anions from the supporting electrolyte, is incorporated in the polymer layer to compensate the positive charge present along the oxidised polymer chains [3]. A number of polymer structures have recently been synthesised which contain polyanions. This has been achieved mainly by electropolymerising monomers, as pyrrole (Py), in presence of polyanions, which are thereby incorporated into the polymer matrix [4-8]. The incorporation of negatively charged molecules is driven electrostatically by the positive charges of the oxidised polypyrrole (pPy) chains. Since the pPy chains have a lower redox potential than that of the monomer, the polymeric oxidation and polyanion-compensation occur simultaneously with the electropolymerisation in order to keep the electroneutrality of the film. These "doping" counterions once incorporated into the film cannot be released due to their large size [1,9] forming a polymeric blend polypyrrole-polyelectrolyte. On this way the electroneutrality, during the polymeric reduction, was guaranteed by penetration of cations from the electrolyte into the pPy matrix. The "doping" molecules should have a considerable impact on the bulk properties of pPy films [10]. Changing the size, shape and distribution of counterions, which, to some extent, must spatially separate pPy chains affecting the level of film oxidation and its conductivity, can change the electronic properties of the pPy.

We report here the electrochemical polymerisation of Py in presence of a new polyelectrolyte sodium poly(maleic acid-co-olefin), (PMAco), in aqueous solution. The aim of this work is to evaluate the influence of the experimental conditions used during the electrochemical synthesis on

either: the productivity of the consumed charge (PC, mass of new blend electrogenerated per unit of consumed charge), and the ability to store charge (SC, the electrical charge stored per unit of mass present in the blend). The studied variables were polymerisation potentials, polymerisation times, the concentration of monomer and the concentration of polyelectrolite.

EXPERIMENTAL

Films of the blend pPy + PMAco were prepared from aqueous solutions. The monomer (Janssen) was distilled in vacuum (59 °C, 50 Torr) before use. PMAco (Aldrich with 3% Na content) was used without previous purification and polyelectrolite concentrations are referred to the Na content. The solvent (water) was obtained from a Milli-Q-Reagent water system fed by a Milli-RO4 Water Purification System. Platinum sheets were used as working and counter electrode with areas of 1 cm² and 2 cm² respectively. An Ag/Ag⁺ electrode was used as reference electrode. The electrochemical measurements were performed through a M270 program. The weights of the polymer films were obtained by ex-situ determination, using a Sartorius 4504 MP8 ultramicrobalance (10⁻⁷ gr. precision).

RESULTS AND DISCUSSION

Voltammetric study was performed using a platinum electrode in 0.35 M Py and 4x10⁻⁴ M PMAco, Figs.1.

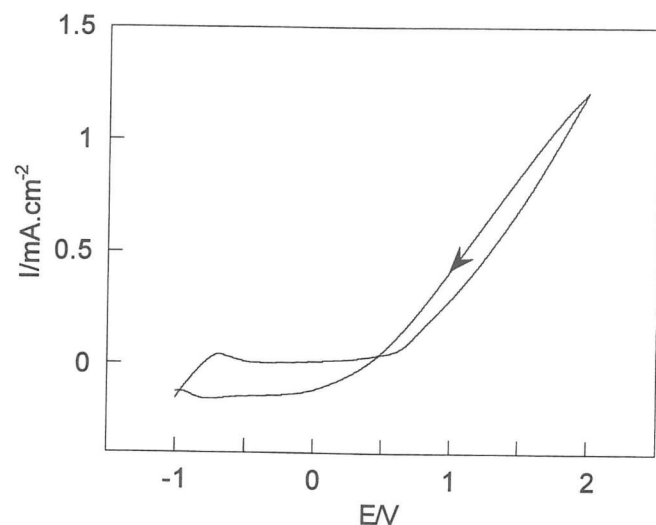


Figure 1: Voltammetric studies between -1.0 V and 2.0 V (Ag/Ag⁺) at 20 mV s⁻¹ a platinum electrode in 4x10⁻⁴ M PMAco + 0.35 M Py aqueous solution.

The oxidation of the monomer began at around 0.5 V. The oxidation-polymerisation process produced a rapid increase of the current density at increasing potentials and the subsequent electrode

darkening. At more cathodic or anodic potentials than -1.0 V or 2.0 V, respectively, a gaseous release is observed from the coated electrode.

Polymerisation at different potentials. In order to investigate the influence of the potential on both, production and properties of the new material, films were prepared by potential steps. A clean platinum electrode was polarised at 0.0 V for 5 s and then the potential was stepped to an anodic potential in the range between 0.8 V and 2.0 V which was kept by 250 s. The procedure was repeated to different anodic potentials inside the range. The initial potential of the step was chosen owing to the inactivity of the system on this potential (Figs.1). Charges consumed during polymerisation were obtained by integration of each experimental chronoamperograms. Once coated, each electrode was rinsed with ketone, dried and weighed. Films generated at different anodic potentials were studied in 0.1 M LiClO₄ aqueous solution by cyclic voltammetry between -0.8 V and 0.2 V at 20 mV.s⁻¹. In order to obtain the electrical charge stored in each film every voltammogram was integrated. Productivity and specific charge as a function of the potential of generation are shown in Figs. 2.

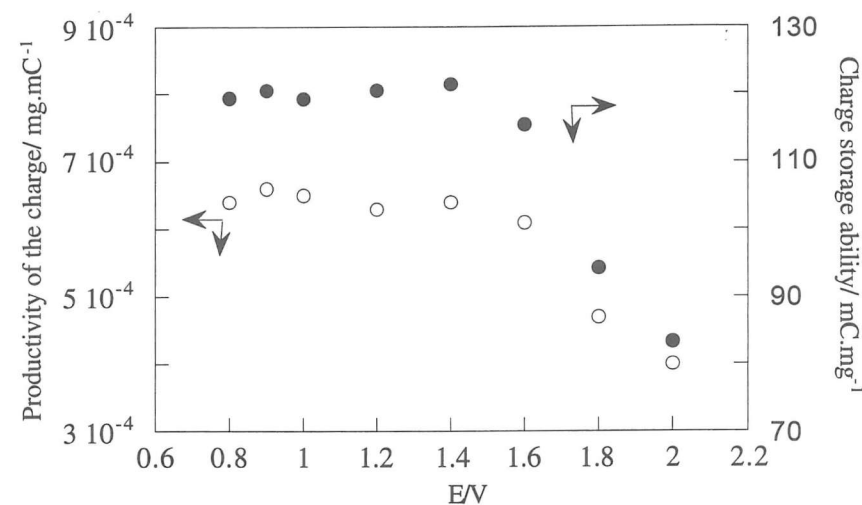


Figure 2: Evolution of the PC and the SC as polarisation potential function to the blend polymerisation in 0.35 M Py + 4.2x10⁻⁴ M PMAco. Polymerisation time: 250 s.

As can be observed, both properties are kept almost constant from 0.8 V to 1.6 V. At higher anodic potentials of generation both magnitudes decrease. A constant productivity points to an unchanged mechanism of polymerization. The decrease observed at higher potential points to the presence of side reactions consuming charge without any production of polymer. Parallel decreasing values observed on the SC indicate that a fraction of this charge is consumed to degrade the polypyrrole. Under our experimental conditions the higher PC and maximum SC are obtained by electrogeneration at lower potential than 1.4 V. Therefore, a potential of 1.2 V was chosen in order to

study the influence the other experimental variables.

Polymerisation at different times. The platinum sheet was submitted to a potential step from 0.0 V to 1.2 V for different polarisation times ranging between 50 and 400s. A fresh 0.35 M Py and 4×10^{-4} M PMAco aqueous solution was used to electrogenerated every one of these films. The procedure was similar to that applied above. Only small variations of PC and SC were observed as a function of the polymerisation time. Those facts suggest that the polymerisation mechanism does not change at different polymerisation time. Taking into account those results and that the low current densities flowing through the system force to long polarisation times in order to get films thick enough to be followed gravimetrically, times longer than 200 s were chosen.

Polymerisation at different concentrations of Py or of PMAco. Polymeric films were electrogenerated in 4×10^{-4} M PMAco aqueous solutions having different monomer concentrations by polarisation at 1.2 volts for 250 s. The experimental procedure was similar to that used when the electric potential was changed. A constant productivity of 6×10^{-4} mg.mC⁻¹ was obtained. This results indicate that the polymerisation mechanism is constant. However, the SC present some variations from 80 mC.mg⁻¹ in film obtained from 0.05M Py until 120 mC.mg⁻¹ in those generated from monomer concentration higher than 0.3 M. In order to get the higher electroactivity in the generated films, monomer concentrations between 0.3 M and 1 M were used. Under those conditions a uniform PC and SC were obtained.

Following a similar experimental procedure keeping now a constant 0.35M monomer concentration the influence of the PMAco concentration on both, productivity of the current and specific charge was studied. Experimental results can be observed on Table 1.

Table 1: Magnitudes related to blend film electrogenerated from 0.35 M Py aqueous solutions with different concentrations of PMAco at constant potential (1.2 V) during 250s

| [PMAco]/ M | [Py]/[PMAco] | 10 ⁴ PC/ mg.mC ⁻¹ | SC/ mC.mg ⁻¹ |
|----------------------|--------------|--|----------------------------|
| 1.4×10^{-4} | 2500 | 4.8 | 150 |
| 4.2×10^{-4} | 834 | 5.0 | 145 |
| 1.4×10^{-3} | 250 | 8.2 | 108 |
| 2.8×10^{-3} | 125 | 8.7 | 100 |

Increasing productivities and decreasing specific charges were obtained when the concentration of the polyelectrolite rises. The opposite shift of those magnitudes points to the presence of increasing adsorption rates of the polyelectrolite ahead that required to keep the electroneutrality in the film during the polymerisation. The PMAco present in film electrogenerated from higher concentrations of electrolyte. This hypothesis seems supported by the low SC in films generated at high PMAco concentrations (Table 1) due to the non-electroactivity of the polyelectrolite.

CONCLUSIONS

A polymeric blend pPy-PMAco can be synthesised by electrochemical polymerisation of

pyrrole in presence of poly(maleic acid-co-olefin) on platinum electrodes. Aqueous solutions having [Py]/[PMAco] ratios higher than 250, ambient temperature, electrodic potentials equal or lower than 1.2 V, and high polymerisation time ($200 \text{ s} \leq t \leq 400 \text{ s}$) were experimental conditions giving fast polymerisation rates (6×10^{-4} mg.mC⁻¹) to produce blends storing a high specific charge (120 mC.mg⁻¹).

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