

If the adsorbate is 4-MP in water or acid media, the monolayer of gold oxide is removed as well. The resulting electrode inhibits the UPD of copper. The UPD process is more inhibited than when 4-MP is adsorbed on oxide free gold. This is because the potential of the interface AuO-4-MP is more favourable for the 4-MP adsorption than the potential of the interface Au-4-MP.

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ELECTROPOLYMERIZATION IN SOLUTION:

AN ELECTROCHEMICAL METHOD TO OBTAIN POLYACRYLAMIDE

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SUMMARY

The electropolymerization of acrylamide in the presence of NaNO₃ in aqueous solution has been investigated on platinum electrodes. The polymer (polyacrylamide) is obtained in the bosom of the solution. The dependence of yields and molecular weights on parameters such as current density, monomer concentration, electrolyte concentration and temperature was determined.

Key words: Electropolymerization, acrylamide

INTRODUCTION

The pass of a electric current between two metallic electrodes sumerged in a monomeric solution with a salt can generate, among other products, polymer adhered at the electrode surface¹ or, in other way, in the bosom of the solution². This last type of polymerization has been considered in literature like a homogeneous initiated process³. Nevertheless, a few authors proposed the formation of polymer films around the electrode during the initial minutes of current flow³. All of this allows us to suppose that the reactions on the electrode are determinant in the electroinitiated polymerizations. The electrode process is a mixed process in which all

species present take part. The relative rate of these process is changed with the variation of the polymerization conditions and along the polymerization time. So, the study of the kinetic of the overall polymerization process becomes more difficult than usually homogeneous polymerization.

EXPERIMENTAL PART

The experimental techniques and apparatus were similar to those described in a previous paper⁵.

RESULTS AND DISCUSSION

There are, in literature, a lot of works about electropolymerization in solution^{6,7,8}. Usually, the range of current density employed is low^{9,10}, until 20 or 25 mA.cm⁻². Wide range of current density were studied in our laboratory using a iridium sheet as working electrode¹¹. A "bell" shape of the conversion evolution at increasing current densities is obtained: at lower current densities conversion rises with the increase of the current density (zone 1), reaches a maximum value between 20 and 30 mA.cm⁻² (zone 2) and decreases at higher current densities (zone 3).

Now, using a platinum wire as working electrode, only the zone 3 is obtained (fig.1) because the range of current densities employed begins at 30 mA.cm². Decreasing conversions at increasing current densities can be related to rising concentrations of initiators around the electrode. That promotes an increase on the initiation rates ($R_{prop} = K_{prop} [M][M']$), but, at the same time the termination rates increases as well, due to increasing concentrations on initiator and polymeric radicals ($R_t = K_t [M']^2$). The final result is a decrease of the polymerization rate.

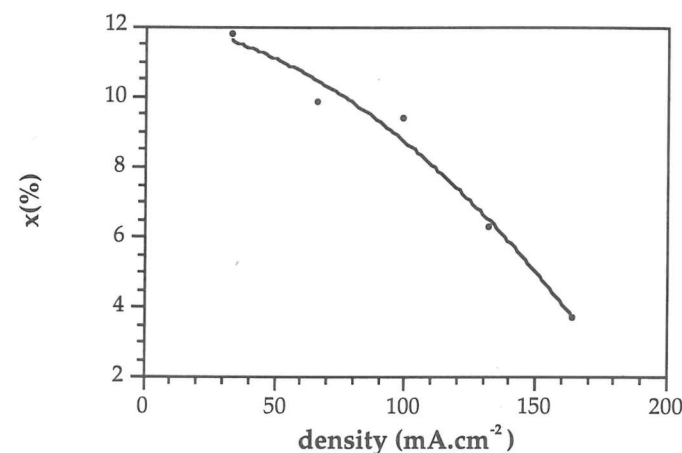


Figure 1: Variation of the monomer conversion with current density. [M] = 3M; [NaNO₃] = 0.3M; T = 35°C; polymerization time=2h.

When the main chemical variables (monomer and electrolyte concentrations) are studied, figure 2 is obtained:

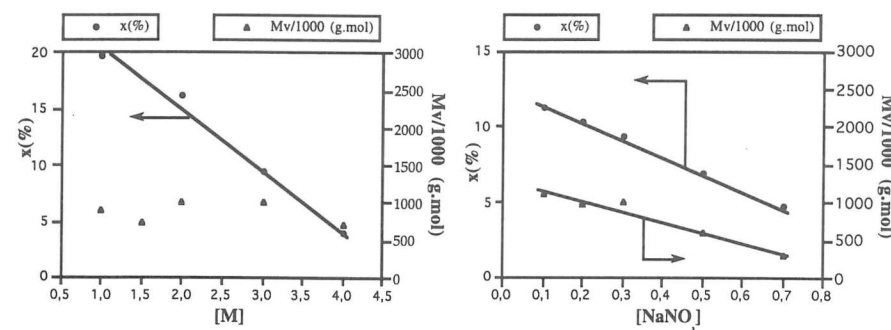


Figure 2: Variation of the conversion and the average viscosimetric molar mass (obtained after 2h of polymerization) when the monomer and electrolyte concentration is changed. j=100mA.cm⁻²; T = 35°C.

This figure shows the evolution of the conversion and the viscosimetric molar mass with the change of monomer concentration (left graph) and electrolyte concentration (right graph). The decrease of

conversion obtained in both cases is related to the increase of the radicals. On the other hand, the decrease of the viscosimetric molar mass obtained when the electrolyte increases points to a predominance of the termination process due to the increase in concentration of monomer radicals. When the monomer concentration is changed, an approximately constant evolution of the molecular weight is observed due to an equilibrium between the increase of the number of monomer molecules (which promotes a rise on the propagation rate) and that of the radicals (which increases the termination rate).

The influence of the temperature was also studied (fig.3).

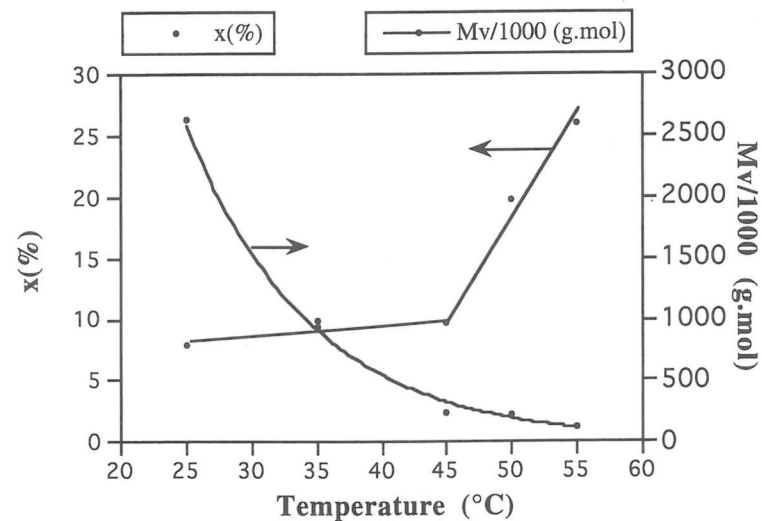


Figure 3: Variation of the conversion and the average viscosimetric molar mass (obtained after 2h of polymerization) when the temperature is changed. [M] = 3M; [NaNO₃] = 0.3M; j = 100mA.cm⁻²; polymerization time=2h.

The average molar mass decreases exponentially with temperature. The higher mobility of the molecules promotes a faster termination of the chains, and so a lower molecular weight.

The evolution of the conversion shows two different temperature regions. While in the first region a low slope is observed, in the second (from 45°C) the conversion rises very quickly with temperature. The electrochemical polymerization coexists with a chemical polymerization (thermal and proton initiated). The relative influence of the chemical way begins to be significant at higher temperatures than 40°C¹². This will be subject of a future publication.

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