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Electrochemical Polymerization of Pyrrole from Aqueous Solutions: 2. Growth Kinetics of Polypyrrole *p*-toluenesulfonate Film

Eui Hwan Song and Woon-Kie Paik *

Department of Chemistry, Sogang University, Seoul 121-742

Jung-Kyoon Chon

Department of Chemistry, Hankuk University of Foreign Studies, Seoul 130-791. Received October 26, 1989

The rates of electropolymerization of pyrrole from aqueous solutions containing *p*-toluenesulfonic acid were studied as functions of the concentration of the surfactant anions and of temperature for the polymerization on the electrode surface immersed in the solution and also for the polymerization along the solution surface. In the case of the *solution-surface polymerization*, the polymerization rate showed maximum as the concentration of the *p*-toluenesulfonic acid changed at a fixed temperature or as the temperature was varied at a fixed concentration. The decrease of the polymerization rate with increasing concentration or with rising temperature beyond the values at the maxima is interpreted as resulting from micelle formation.

Introduction

In recent years, there have been numerous investigations¹⁻⁹ on the electropolymerization of pyrrole in various solvents to obtain polypyrrole which is electronically conducting when anodically "doped" with anions. Polypyrrole (PPy) films incorporated with surface-active anions have recently received considerable interest because of the enhanced mechanical and conducting properties¹⁰. In a previous communication¹¹ we reported that polymerization of pyrrole can occur not only on the surface of an electrode immersed in the solution (*in-solution polymerization*) but also along the solution surface when the electrode is placed horizontally touching on the surface of the solution (*solution-surface polymerization*). The *solution-surface polymerization* was achieved by using an aqueous pyrrole solution containing surfactant anions, such as *p*-toluenesulfonic acid (*p*-TSA) and sodium dodecylsulfate. The polymer obtained by the

solution-surface polymerization was in the form of thin film attached on both sides of the platinum wire or in the form of fibrillar bundles depending on the electrolytes used. The polypyrrole film obtained by the *solution-surface polymerization* method using *p*-toluenesulfonic acid (*p*-TSA) had improved mechanical and conducting properties in comparison with the ones obtained by the *in-solution polymerization* method, although the structural units of the conducting polymers obtained by the two methods were both approximately [(Py-Py)⁺A⁻].

In this paper, we report our results of a comparative study on the growth rate of the polypyrrole *p*-TSA films by the *in-solution polymerization* and the *solution-surface polymerization* techniques.

Experimental

Pyrrole (from Fluka) was purified by vacuum distillation

over calcium hydride¹². The clear pyrrole thus obtained was stored under nitrogen atmosphere in a dark cold room at 4 °C until use. *p*-Toluenesulfonic acid (*p*-TSA, from Aldrich) was used as the supporting electrolyte without further purification. All electrolyte solutions were prepared with doubly distilled water whose conductivity was less than 10^{-7} ohm⁻¹cm⁻¹.

The electrochemical measurements were carried out with a Princeton Applied Research (PAR) model 173 potentiostat/galvanostat, a model 179 digital coulometer plug-in and a model 175 potential programmer. For the electrochemical cell, we employed a dual compartment cell with the three-electrode system. A fine porosity glass frit was used to separate the working electrode compartment from the counter electrode. A platinum wire (geometric surface area = 0.24cm²) and a Pt plate (geometric surface area = 3.4cm²) were used as the working electrode for the solution-surface polymerization and the in-solution polymerization methods, respectively. Prior to use, the platinum plate was polished with slurry of alumina polishing powder of 0.1 micron. The reference electrode was a saturated calomel electrode encased in a tube with a Luggin probe. The potential data given here are referred to this electrode. The solutions were deaerated with stream of nitrogen which had been purified by passing through a tube of hot copper shreds, and all measurements were performed under the nitrogen atmosphere. Most of the experiments were performed at room temperature. However, for the investigation of the temperature effect on the polymerization rate, the electrolysis cell was immersed in a water bath whose temperature was controlled by a proportionally regulated thermostat within 0.1 degree.

Results and Discussions

By means of the in-solution polymerization method, a solid conducting polypyrrole coating on the immersed electrode surface was obtained, and by the solution-surface polymerization method a free-standing film of the conducting polypyrrole in the form of a round plate was grown. The anodic charges consumed during the polymerization using the solutions of *p*-toluene sulfonic acid (*p*-TSA) per unit geometric area of the electrode are plotted in Figure 1. The solution used for the measurements presented in this paper was 0.2M pyrrole plus 0.1M *p*-TSA and the temperature was 25 °C except when noted otherwise. The anodic charge is a direct measure of the extent of polymerization because there is little faradaic side reaction besides the electropolymerization; *i.e.*, the current efficiency is near 100%. The slopes of the charge vs. time curves in Figure 1, corresponding to the polymerization currents, represent the polymerization rates, and are presented in Figure 2 as functions of time. Both Figures 1 and 2 show that the polymerization becomes increasingly faster in the case of solution-surface polymerization while in the case of in-solution polymerization the rate increases only slightly. In these two figures, a direct quantitative comparison between the polymerization rates of the solution-surface and the in-solution polymerization is not possible because the geometries of the electrode surfaces at which the reactions take place are not equal. Only the relative change of the polymerization rates of the two

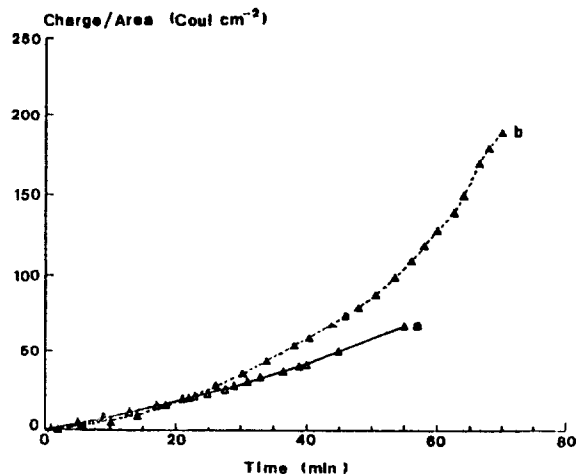


Figure 1. The anodic charge vs. time of electropolymerization of pyrrole at the electrode potential of 0.7V vs. SEC in the 0.1M *p*-TSA and 0.2M pyrrole solution. (a) in-solution polymerization; (b) solution-surface polymerization.

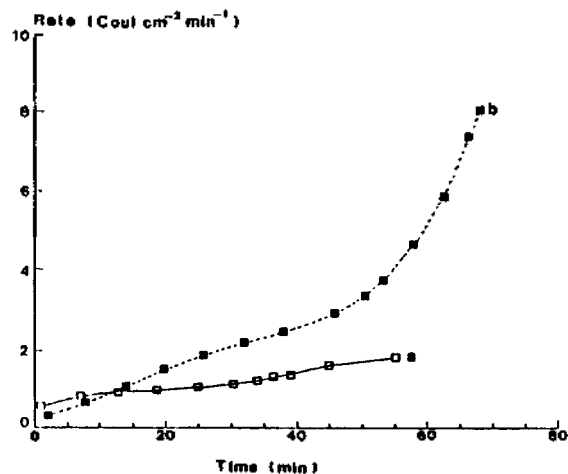


Figure 2. The polymerization rate as expressed by the rate of increasing anodic charge with time. (a) in-solution polymerization; (b) solution-surface polymerization.

polymerization modes are to be compared. Even if an identical electrode were used for the two modes of polymerization, because the polymer growth by the solution-surface polymerization take place along the gas-solution boundary instead of on the electrode surface as in the case of the in-solution polymerization, the real area of the effective electrode surface becomes different than that of the in-solution polymerization. At the beginning of the polymerization the rate figures provide a basis for comparison even though electrodes of different geometries are used since the rates are expressed for unit surface area.

The gradual increases of the growth rates can be attributed to increasing surface reaction sites due to expansion of the surface area and roughening of the surface. At the beginning of the polymerization, the metal electrode surface acts as the catalyzing substrate, but as the solid polymer grows over the metal surface the polymer surface replaces the metal surface as the catalyzing substrate for further polymerization. Thus, the polymerization is autocatalytic in a

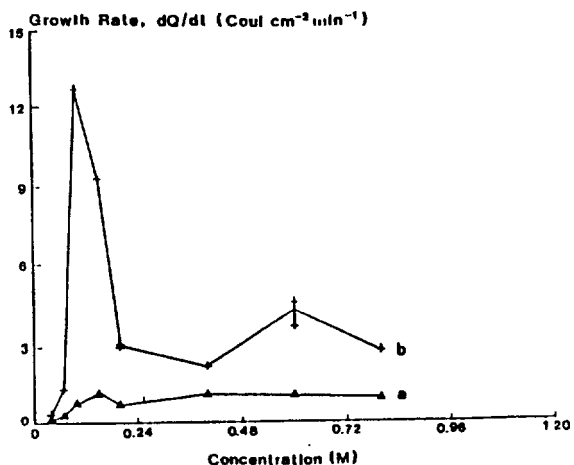


Figure 3. The rate of polymerization at different concentrations of *p*-TSA. The rates are measured at 30 min. of electrolysis time. (a) in-solution polymerization; (b) solution-surface polymerization.

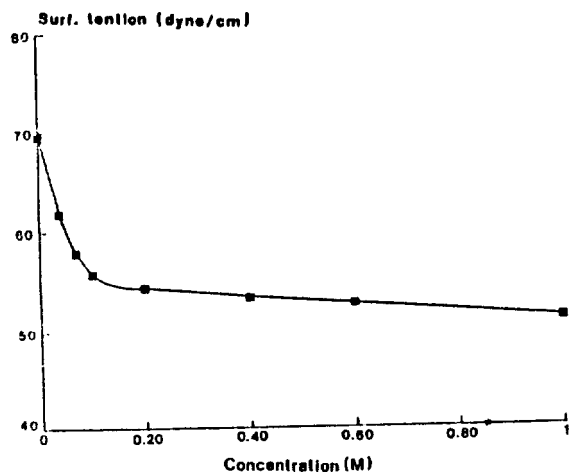


Figure 4. Surface tension of *p*-TSA and 0.2M pyrrole solution measured at various concentrations of *p*-TSA.

sense. In the case of the solution-surface growth, there is increase of the circumference of the polymer plate, along which the growth occurs predominantly. This increase of the circumference seems to be more important than the increase in the roughness factor in bringing about the increase of the growth rate.

In order to investigate the effect of concentration of the surface active agent, the polymerization rate was measured with different concentrations of *p*-TSA. Because the rate changes gradually with time, the rates were measured at 30 min of electrolysis time in all cases. The polymerization rates measured at various concentration of *p*-TSA are shown in Figure 3. The in-solution polymerization rate appeared to be little affected by the concentration except at low concentrations below 0.1M (Figure 3). The rate of solution-surface polymerization, however, showed a sharp maximum at a concentration of about 0.1M. We measured the surface tension of the surfactant solutions containing pyrrole by the ring-balance method, the result of which is shown in Figure 4. The steep decrease of the surface tension with increasing concentration of the surfactant halts at about 0.1M, which approximately coincides with the concentration of maximum

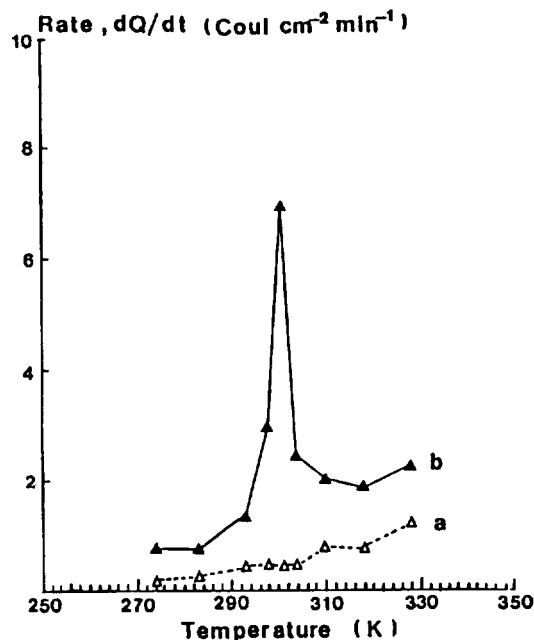


Figure 5. Polymerization rates at different temperature for the in-solution polymerization (a), and the solution-surface polymerization (b). The rates were measured at 30 min. of electrolysis time.

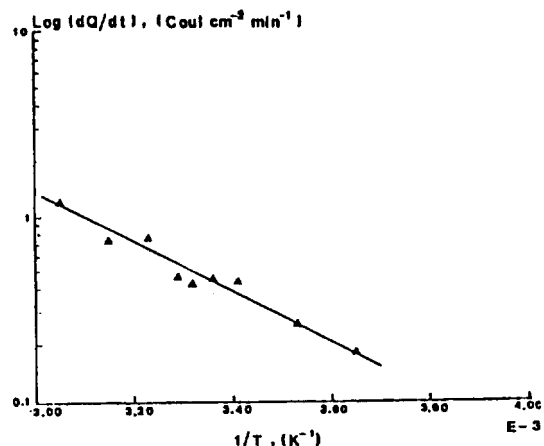


Figure 6. The arrhenius plot for the rate of in-solution polymerization. The rates were measured at 30 min. of electrolysis time.

growth rate by the solution-surface polymerization. We, therefore, consider the steep decrease of the polymerization rate beyond the maximum to be related to the micelle formation from the surface active anions. Thus, the sharp peak in the rate-concentration curve in Figure 3 suggests an enhancement of the rate as the concentration of *p*-TSA approaches the critical micelle concentration(CMC) and a retarding mechanism beyond the CMC. The small second rise in the rate curve for the solution-surface polymerization resulting in a minor peak is not understood at present.

The growth rate of the polypyrrole in the *p*-TSA solution increased with the rise in temperature (Figure 5). The Arrhenius plot for the in-solution polymerization is shown in Figure 6, from which an apparent activation energy of approximately 0.26 eV is obtained. In the case of solution-surface growth, however, there was a striking maximum in the rate

vs. temperature curve above the room temperature as shown in Figure 5. Here again, the rate data are the ones taken at 30 min of polymerization.

If a same polymerization mechanism were assumed for both the in-solution and the solution-surface polymerization processes, the appearance of the maximum in the rate vs. temperature relation in the case of solution-surface polymerization seems to be strange. Mechanisms proposed for the electropolymerization of pyrrole in the literature^{2,4,13} usually assumes one-electron transfer steps. A recent electrochemical study¹⁴ indicated a sequence of two-electron transfer steps. None of the proposed mechanisms would predict the peculiar maximum in the rate vs. temperature relation. An explanation for this apparent anomaly may also be found in the assumption of micelle formation. The micelle formation is known to be entropy-driven: the enthalpy of micellization is usually close to zero and at times is positive, and the entropy of the system *increases* as the micelles are formed due to the structure breaking of hydration water around the ions^{15,16}. Also, the enthalpy of micelle formation becomes increasingly negative with rise in temperature¹⁷. Therefore, the free energy of micelle formation can decrease with rising temperature. In fact, there are numerous instances of the CMC's *decreasing* with rising temperature¹⁸. Supposing that the anions were not aggregated at the room temperature and at the concentration used in the experiment, micelles may start to form as the temperature is raised, and hence the polymerization may be retarded as it is with increasing concentration of *p*-TSA.

Explanation of the sharp rise in the solution-surface polymerization rate as the conditions for micelle formation are approached and of the steep decrease in the rate beyond the point of maximum may be found in the fact that the micelles are bulky and their surfaces are negatively charged, the charges being balanced by the counter ions. For the conducting polymer to grow, the polymer backbone needs to be coordinated by anions around its positively charged nitrogen atoms. Because there are surface excesses of the *p*-TSA molecules and the *p*-TSA anion at the gas-solution interface, barring the micelle formation, the growth rate will be faster at the surface as evidenced by the higher polymerization rate in the case of solution-surface polymerization in comparison to the in-solution case. The rate should increase rapidly with the increase of concentration of the surface-active anions because the surface excess also rises sharply with the bulk concentration. However, once the micelles start to form, the negatively charged micells may attach themselves to the edges of the solid polymer, and retard the growth by steric hindrance to the access of the monomers and anions to the polymer edge. The micelles are too bulky to be incorporated into the polymer as the "dopant". Another possible inhibition mechanism of the polymer growth by the micelle formation is inclusion of the pyrrole monomers in the interior of micelles, and hence reduction of the monomer concentration in the aqueous phase. In view of the fact that pyrrole has limited solubility in water while it is more soluble in organic

solvents, the inclusion of pyrrole in the micelles is quite probable. It seems to present a subtle problem to understand the reason why the polymerization rate is so profoundly affected by the micelle formation in the case of the solution-surface growth while it is not in the in-solution growth case. The *p*-TSA anions, being surface-active, are positively adsorbed at the gas-solution interface. It is therefore possible that the effects of the anions and their micelle formation are more profound at the solution surface.

However, much of the above explanations of the anomalous concentration- and temperature-dependence of the polymerization rate are based upon conjectures and, therefore, need to be substantiated by further investigations. Works on this line are being carried on in this laboratory.

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