Quartz Crystal Microbalance Study for Chemical Synthesis of Polypyrrole

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SYNOPSIS

The quartz crystal microbalance was used to monitor the deposition of a smooth film of the conductive polypyrrole (PP) using a purely chemical method. The film was grown from the oxidative polymerization of pyrrole with potassium persulfate in aqueous solution. A comparison was made between the growth rate of PP films and the PP formed in the bulk at the same molar ratio of the reactants. The kinetics of the PP film formation were found to be governed by the concentration of the reactants in the bulk. The effect of HCl on the growth rate of PP films was also investigated. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, polypyrrole (PP) has been the focus of many studies because of its electrical conductivity and its high air stability in comparison to the other conductive organic polymers.[1] It is well known that PP can be prepared by either electrochemical[2-4] or chemical methods.[5-7] However, the mostly common route for the synthesis of PP films is electrochemical. The electrochemical technique requires that the film be grown on a substrate that is itself conducting. In addition, the deposition of these films having uniform thickness on a topographically complex surface is extremely difficult. For these reasons, purely chemical methods for the preparation of films of PP are receiving increasing attention. The large majority of the earlier studies on the chemical synthesis of PP, however, has focused on the formation of the "pyrrole black" powders formed in the bulk solution.

In one earlier work, insulating films of this polymer were formed on the free surface of a solution containing pyrrole in an ethanol–water–sulfuric acid solution.[8] These films could be made conducting by halogenation or by standing in ambient. More recently, PP films were synthesized from aqueous and water–toluene solutions[9] in the presence of a variety

of oxidizing salts. The films studied were those obtained $FeCl_3$ as an oxidizing agent. These films were resulted in rather rough, granular films. These films had formed both on the free surface of the liquid and on the surfaces of the containing vessel. Scanning electron micrographs of these films showed them to be quite rough.

In an earlier study[10,11] we described the deposition of smooth, adherent films of PP using a purely chemical route from an aqueous solution that contained $FeCl_3$ as an oxidizing agent. These films were monitored using the quartz crystal microbalance (QCM). The growth rate on one of its gold electrodes appeared to be controlled by the bulk concentrations of the reactants through a second-order process. It has been shown also that PP films were able to be chemically formed on a number of conducting and insulating substrates. The variety of surfaces suggests that the formation of these PP films is quite a general phenomenon, providing another degree of flexibility for the use of such conducting polymers.

It has been mentioned that pyrrole can be oxidatively polymerized by potassium persulfate ($K_2S_2O_8$) in aqueous media to form pyrrole black.[12] The formed PP in the bulk solution was affected by the initial concentration of the reactants. In this study we would like to study the same polymerization using QCM technique. The purposes of using this technique are: (i) to study the formation of a highly conducting PP film for possible practical ap-

plications, (ii) to determine the kinetics of PP film formation, and (iii) to justify the assumption that the growth rate of polymerization on the surface is governed by the bulk process.

EXPERIMENTAL

The pyrrole was obtained from Aldrich Chemicals and was purified by passing through a column of alumina neutral. $K_2S_2O_8$ was from BDH chemicals and used as received. In a typical preparation, 200 mL of 9.44×10^{-4} M solution of pyrrole was added to 200 mL of 1.89×10^{-3} M solution of $K_2S_2O_8$. In this case, when mixed, the molar ratio of $S_2O_8^{2-}$ to pyrrole would be 2 : 1.

These solutions were premixed and stirred to ensure homogeneity, then added to the polypropylene bottle shown in Figure 1. A hole had been made in the cap of the bottle and a 5-MHz AT-cut quartz resonator, 1 inch in diameter; covered this hole, sealed with silicon rubber, as shown in Figure 1. This resonator formed the frequency-determining element for an electronic oscillator. The frequency was measured using a Fluke/Phillips PM 6654 frequency counter. Special care had to be taken to ensure the quality of the signal. Details of the apparatus design are described in an earlier study.[10] It was necessary

to ensure that the temperature of the solution to be added was the same as that of the enclosure at 20°C.

It is possible to account for remaining frequency effects resulting from interfacing the crystal with the liquid solution in a quantitative manner. The acoustic shear waves excited by the resonator generates acoustic waves in the liquid, which are strongly damped due to the viscosity. The damping absorbs energy from the shear waves, and if severe enough, can cause a cessation of oscillation. Oscillator circuitry designed to compensate for these losses minimizes this problem. The motions of the damped shear wave in the liquid also induces a change in the resonant frequency described by[13]

$$\Delta f = - \frac{f_0^{3/2}}{\sqrt{\pi \rho_Q \mu_Q}} \sqrt{\rho_1 \eta_1} \tag{1}$$

where f_0 is the unloaded frequency of the resonator, ρ_Q is the quartz density, μ_Q is the piezoelectrically stiffened shear modulus for the quartz, ρ_1 is the liquid density, and η_1 is its viscosity. It was assumed that the variation of these parameters is negligible during the experiment so the change in the frequency due to this effect can be considered constant. In addition, the liquid can be entrained in pockets of localized roughness on the surface. Again, it is assumed that the topography remains constant during the course
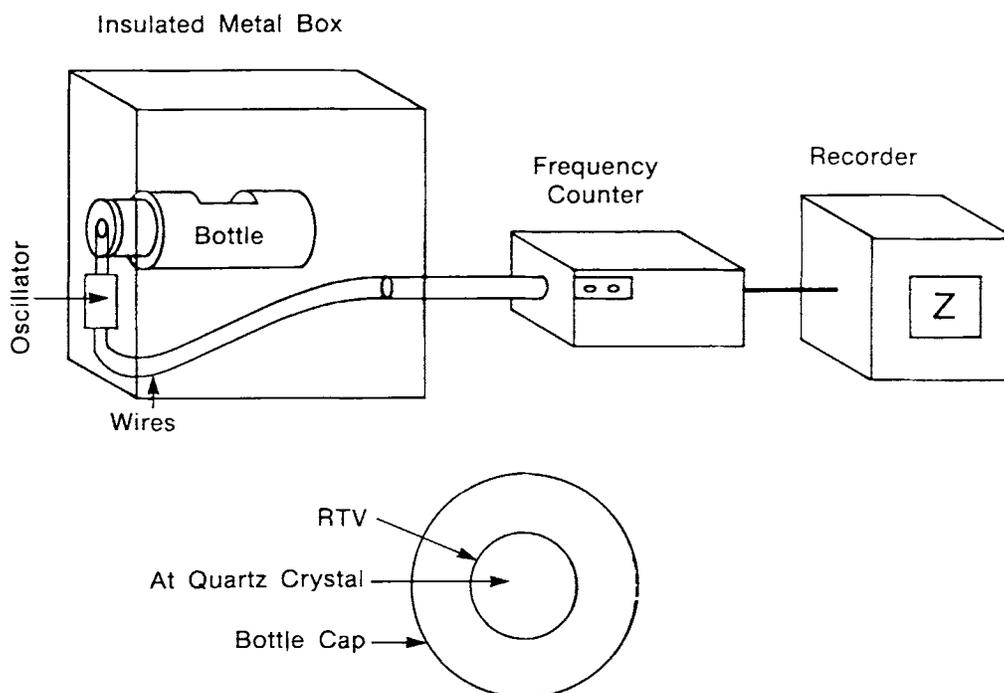

Figure 1 A sketch of the experimental arrangement, including the crystal mounting.

of any given experiment resulting in a constant frequency shift. The frequency shift of interest is that due to the deposition of PP on the surface. The mass per unit area deposited on the crystal can be calculated from the frequency change of the resonance using the Sauerbrey[14] equation:

$$\Delta f = -\frac{2f_0^2}{\sqrt{\rho_Q \mu_Q}} m' \qquad (2)$$

The quartz density ρ_Q has the value 2.649 g/cm^3, the shear modulus μ_Q has the value 2.947 × 10^{11} dyn/cm^2, and m' is the mass per unit area. The thickness of the films can easily be calculated from the mass per unit area since $m' = \rho \epsilon$ where ρ is the density of the film and ϵ its thickness. The density value of 1.5 for the PP was taken from the average of the flotation densities of a number of electrochemically generated films of PP.[2] Using Eq. (2), it can be shown that 150 Hz corresponds to a thickness of 185 Å of PP. The rate of growth is easily calculated then from the slope of the thickness–time relation.

During the growth, the solution was not stirred. Earlier experiments have shown that stirred solutions increased the number of bulk-generated particles on the surface of the crystal. Further, the vertical orientation of the crystal was also chosen to minimize the adherence of these particles. After the growth, the exposed face was then gently rinsed many times with ethanol and distilled water and then dried. The crystal with its adherent PP film could then be used for other studies such as scanning electron microscopy.
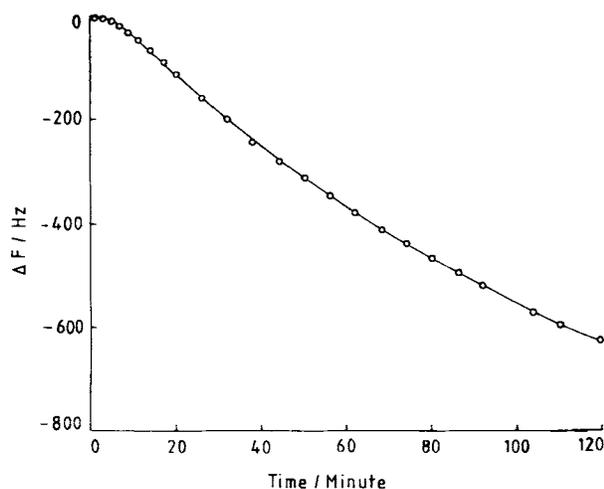
Figure 2 shows the plots of the frequency change

Figure 2 Frequency change (Δf) as a function of time during the polymerization of pyrrole.

(Δf) as a function of time. Three regions of the deposition process are seen. Initially the first deposits of PP must nucleate on the gold surface and give rise to a rather slow incubation for the deposition. It was found that solutions at low concentrations gave rise to behavior showing long incubation times, while solutions at high concentrations yielded unobservably short incubation times. Stirring was also found to decrease the incubation time. Following this incubation period, the growth rate is seen to increase, as evidenced by the increasing magnitude of the slope and then to decrease again as the deposition proceeds. The decrease in the rate at longer times is believed to be due to the depletion of the reactants. For film thickness greater than about 100 Å the incubation has been completed while the concentration of the reactants is believed to be still close to the initial concentration. For that reason, we have chosen the growth rate in the range from 100 to a few hundred Å to characterize each run.

RESULTS AND DISCUSSION

In previous work,[10] we studied the PP film formation using FeCl$_3$ as an oxidizing agent. It is worth noting that when a given concentration of pyrrole solution in water was added to an aqueous solution of FeCl$_3$ or S$_2$O$_8^{2-}$ at the same concentration and temperature, the growth rate of the film deposition was rapid in the case of S$_2$O$_8^{2-}$.

Potassium persulfate is a strong oxidizing agent and has been used in the oxidation of a large number of organic compounds. The redox potential of the persulfate decomposition

$$S_2O_8^{2-} + 2e \rightleftarrows 2 SO_4^{2-}$$
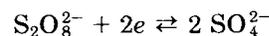
is estimated to be 2.01 V. Furthermore, the persulfate ion is a good initiator. A detailed mechanism for the initiation by persulfate ion to the polymerization process has been discussed elsewhere.[15]

In the present study, a series of experiments were made in which a pyrrole concentration was kept constant at 0.0045 M (200 mL) and varying concentrations of S$_2$O$_8^{2-}$ (200 mL) were added to pyrrole solution. The molar ratio between S$_2$O$_8^{2-}$ and pyrrole varies from 0.1 : 1 to 10 : 1. The growth rate of PP film for each solution was measured as described above. Figure 3 shows the plots of the growth rate of PP films against the molar ratio of S$_2$O$_8^{2-}$–pyrrole. It can be seen that the rate increases as the concentration of S$_2$O$_8^{2-}$ increases up to a
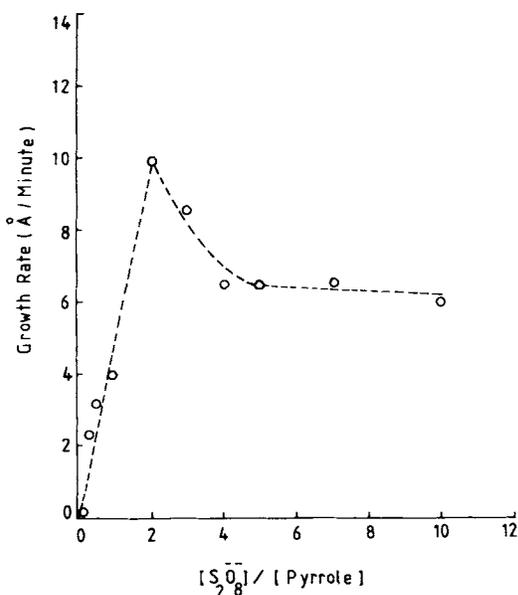
Figure 3   Growth rate of PP films as a function of the molar ratio of the reactants.

maximum when the ratio of $S_2O_8^{2-}$-pyrrole reaches 2. This was followed by a decrease in the rate as the concentration of $S_2O_8^{2-}$ increases. Similar behavior was obtained by Starkweather et al.[16] in the polymerization of styrene. It has been suggested that the persulfate acts not only as initiator but also as a retarder.[17]

In order to study the kinetics of PP film deposition in the present work, an assumption was proposed: The growth rate of PP on the surface is proportional to the rate of formation of PP in the bulk. This assumption can be justified by a comparison between our results and those obtained by Khulbe et al.[12] during the preparation of PP in the bulk using the chemical route. They have mixed a fixed concentration of aqueous pyrrole with different concentrations of $S_2O_8^{2-}$ and left the mixture standing for 6 days. Under these conditions, the formation of PP ceased. The yield of PP formed increased as the concentration of $S_2O_8^{2-}$ in solution increased, it reached a maximum when the molar ratio of $S_2O_8^{2-}$-pyrrole was 2. This was followed by a subsequent decrease as the concentrations of $S_2O_8^{2-}$ increased. The plots of PP yield against the molar ratio of $S_2O_8^{2-}$-pyrrole is shown in Figure 4.

It is obvious from Figures 3 and 4 that the pattern of the rate of PP film vs. molar ratio of the reactants is a mirror image of the plot obtained for the PP formed in the bulk vs. molar ratio of the reactants. This indicates clearly that the polymerization on the surface is controlled by that occurring in the

bulk. It is worth noting that the time required to carry out each experiment for different solutions is approximately 2 h. Within this time, the concentrations of pyrrole and $S_2O_8^{2-}$ are still close to the initial concentrations. In spite of this condition, an agreement is obtained between our results and that obtained in the bulk after 6 days.

The reaction order for PP film formation has been studied using the electrochemical techniques. The results were conflicting. Values of the reaction order were obtained by the examination of log (current) vs. log [pyrrole] plots as a function of potential during deposition.[18-20] The ambiguities concerning these results are discussed elsewhere.[21] Recently, Reynolds et al.[21] have used an electrochemical quartz crystal microbalance (EQCM) technique. The kinetics of PP film deposition were determined by the examination of log (deposition rate) vs. log [pyrrole]. It is worth mentioning, however, that the present method in which QCM is used during the chemical oxidation of pyrrole is more convenient, inexpensive, and can be rapid. The difficulty of obtaining PP film of good properties on a conducting or insulating substrate is avoided. Scanning electromicrograph of these films is shown in Figure 5. The surfaces are seen to be fairly smooth.

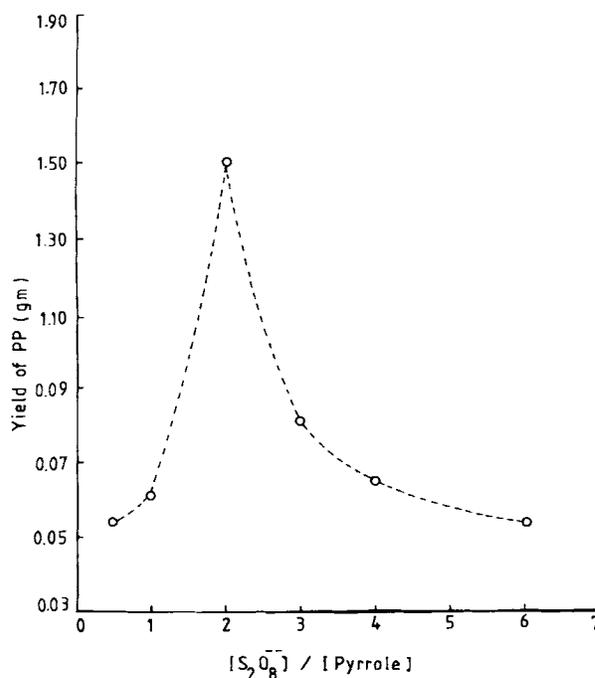The dependence of the growth rate on reactants concentration was determined from the slope of the

Figure 4   Yield of PP formed in the bulk as a function of the molar ratio of the reactants (Khulbe et al. data, Ref. 12.

mass or thickness vs. time plots during polymerization (Fig. 2). These slopes will yield the rate at a given concentration of pyrrole and $S_2O_8^{2-}$. The pyrrole concentration was kept constant at $0.0045M$ and only the $S_2O_8^{2-}$ concentration was varied. The molar ratio of $S_2O_8^{2-}$–pyrrole was changed from 0.1 to 2. The results are plotted in log-log fashion (Fig. 6). A straight line was obtained with slope equal to 1.19. This indicates that the rate is first order with respect to $S_2O_8^{2-}$. On the other hand, the concentration of $S_2O_8^{2-}$ was kept constant at $1.2 \times 10^{-3} M$ and the pyrrole concentration was varied. The molar ratio of $S_2O_8^{2-}$–pyrrole was changed from 2 to 0.2. A straight line was obtained with slope equal to 1.15. This shows that the rate is also first order with respect to pyrrole. Further evidence comes when the molar ratio of $S_2O_8^{2-}$–pyrrole was fixed at 2 and the concentrations of $S_2O_8^{2-}$ and pyrrole were varied. The results obtained are plotted in Figure 7, as log-log fashion, which gives a straight line with slope equal to 1.05. This justifies the kinetics of the growth rate to be first order with respect to $S_2O_8^{2-}$ and to pyrrole and overall second order.

It is reasonable to suggest that both PP films and that formed in the bulk have the same chemical
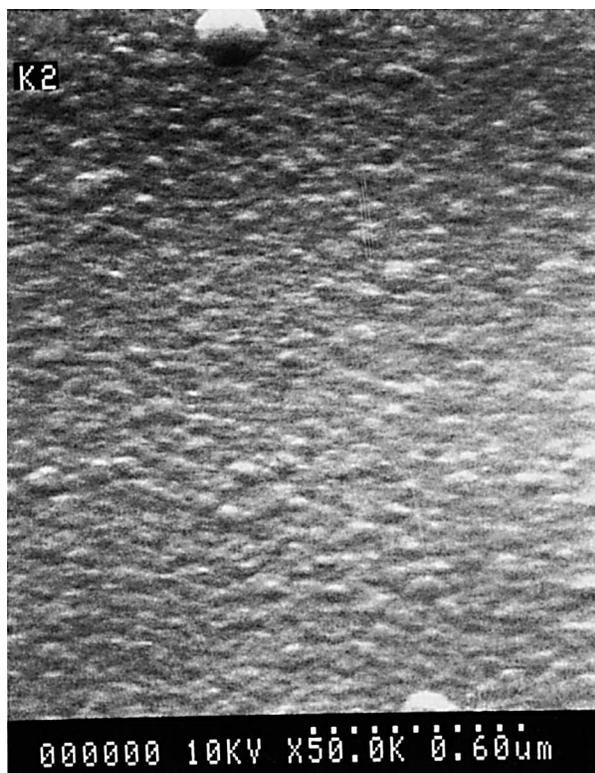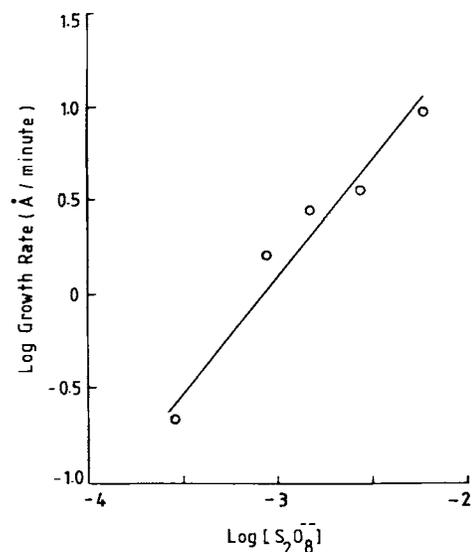
Figure 6   Log-log plot of the growth rate vs. the concentration of the $S_2O_8^{2-}$, the molar ratio of pyrrole–$S_2O_8^{2-}$ vary from 0.1 to 2.

composition. Khulbe et al.[12] have discussed in details the IR spectra and the elemental analysis of PP products at different molar ratio of $S_2O_8^{2-}$–pyrrole. It was concluded that these products are similar to pyrrole black.[5] In addition, on the basis of elemental analysis, the percentage of the basic elements—C, H, N, and O—for the PP formed at different molar ratio of the reactants are very similar. A slight in-
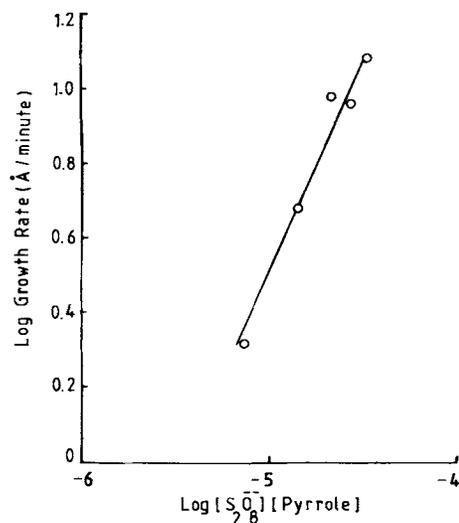
Figure 5   Scanning electron micrographs of PP surface.

Figure 7   Log-log plot of the growth rate vs. the concentration product of the reactants, the molar ratio of pyrrole–$S_2O_8^{2-}$ kept constant at 1 : 2.

crease of the oxygen content was observed when the initial concentration of pyrrole decreased. The average empirical formula was represented as $C_4H_{3.5}NO_{1:2.4}$. This indicates that C : H : N ratio is very close to the theoretical value of 4 : 3 : 1 for oxidatively coupled pyrrole polymer.[8]

It is likely that the polymerization proceeds in a stepwise reaction rather than a chain reaction. This is similar to the mechanism proposed by Inoue et al.[22] for the chemical oxidation of pyrrole with copper perchlorate. At the initial stage of polymerization, the pyrrole radical cation can be initiated, which coordinates with other pyrrole units. It has been suggested that the sulfate radical anion ($SO_4^{\cdot-}$), which generates from the reaction

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-}$$

initiates the polymerization process.

An electrical conductivity measurement was made for a film grown from a solution with a molar ratio of $S_2O_8^{2-}$-pyrrole equal to 2. The measurement was carried out using a four-probe technique as described elsewhere.[10] The conductivity for a film of thickness 340 Å is 0.24 S cm^{-1}. While this is much less than the very high value of 100 S cm^{-1} for the PP grown electrochemically, it is nonetheless a highly conductive film. Further work is in progress to study the electrical properties of these films obtained from different molar ratios of the reactants.

In previous studies,[11] we reported that the growth rate and the conductivity of PP films formed chemically from anhydrous $FeCl_3$ were affected by HCl addition. This is in spite of the fact that HCl is one of the products of the polymerization. In the present study, we would like to see the effect of HCl on the growth rate of PP films formed using the mild oxidizing $S_2O_8^{2-}$ in aqueous media.

Figure 8 shows the results of a set of experiments carried out for solutions having a constant concentration of pyrrole ($0.0045\,M$) and the molar ratio of $S_2O_8^{2-}$-pyrrole equal to 2. Various concentrations of HCl were added ranging from 0.0015 to $0.021\,M$. The rate for a film grown without added HCl is about 9.92 Å/min. It can be shown from Figure 8 that the rate is largely increased by addition of a small concentration of HCl. This rate being 14.3 Å/min at $0.0015\,M$ HCl and 37.03 Å/min at $0.021\,M$ HCl.

It has been mentioned that a fraction of pyrrole monomers are converted to secondary products, such as 2.5-bis-(2-pyrrolyl)pyrrolidine in the presence of HCl.[23,24] It might be, therefore, anticipated that these secondary products may incorporate in the growing film. This may increase the rate. An additional study will be made to study this effect in detail.
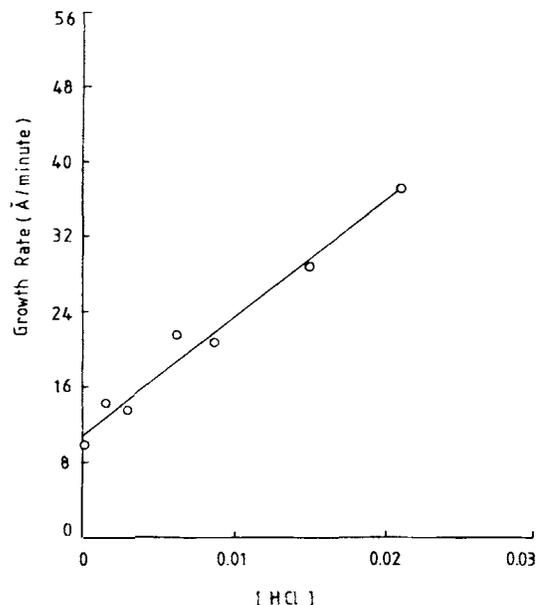

Figure 8 The growth rate for films at initial HCl concentrations as indicated along the abcissa, the molar ratio of pyrrole-$S_2O_8^{2-}$ kept constant at 1 : 2 and [pyrrole] $= 0.0045\,M$.

CONCLUSION

It is shown that QCM technique is an effective monitor for PP films formed chemically. These films are smooth, shiny, and adherent. The growth rate of PP films is governed by the rate of PP formation in the bulk.

The kinetics of PP films grown on the surface were investigated and appeared to be controlled by the reactants concentration through an overall second-order process. This is consistent with the results obtained previously. Finally, it is worth mentioning that the QCM technique concomitant with the chemical route may provide a convenient, economic, and rapid method to study the formation and topography of PP films.

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