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Investigation into vapour-phase formation of polypyrrole

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Vapour-phase chemical polymerization of pyrrole was investigated in which a cotton thread coated with $FeCl_3$ oxidant was exposed to pyrrole vapour and the electrical resistance of this conductive polypyrrole supported on cotton thread was measured using a specially designed four-point probe. The relationships of the resistance of the polypyrrole supported on cotton thread with various experimental parameters such as concentrations of the oxidant and monomer, polymerization time, solvent effect and temperature were studied. It was found that the vapour-phase polymerization was a fast reaction. The resistance decreased with an increasing concentration of $FeCl_3$ and polymerization temperature. The presence of some solvents such as water, hexane and toluene in the vapour phase did not affect the polymerization process. However, some solvents such as methanol and acetone were found to be unsuitable for this process.

(Keywords: polypyrrole; vapour-phase polymerization; resistance)

INTRODUCTION

Among the various conducting polymers, polypyrrole (PPy) has been extensively investigated owing to its numerous desirable properties, e.g. good environmental stability, high conductivity and ease of preparation. PPy can be prepared by either electrochemical or chemical oxidative means. Broadly, the chemical oxidative polymerization can occur via three modes: (i) in a homogeneous solution[1-6]; (ii) at an interphase of two immiscible solutions[7,8]; and (iii) in the vapour phase[6,9-12]. The properties of the PPy, e.g. conductivity, strength and morphology, obtained are very dependent on the conditions and modes of polymerization. Various types of oxidizing agents have been used for chemical polymerization, e.g. copper(II)[13-15], silver(I)[14] and iron(III)[4-6,13-16]. Among them, $FeCl_3$ has been the most extensively used oxidizing agent. When pyrrole is in contact with an oxidant in the liquid phase, a dark, messy solution is formed and a great quantity of waste is generated. This problem may be resolved by vapour-phase polymerization[6,9-12], an area that has been rather neglected.

In vapour-phase polymerization, when a substrate precoated with an oxidant is exposed to pyrrole vapour, PPy will be deposited on the substrate. In comparison with electrochemical polymerization, the vapour-phase and interphase chemical polymerization do not restrict the area of the films, this being a limitation due to the size of the electrode. Moreover, uniformity of the electrochemically prepared PPy film is difficult to achieve.

Many kinds of supporting substrates for the homogeneous chemical polymerization of pyrrole have been used, e.g. rayon[4], nylon[5], filter paper[6] and wood[6]. The variety of substrates used for the vapour-phase chemical polymerization is not as extensive as the substrates mentioned above. Miyata *et al.*[9] and Kise *et al.*[10] used poly(vinyl alcohol) as PPy support in vapour-phase chemical polymerization. They studied the effects of the experimental conditions, such as polymerization time, concentrations of the oxidant and pyrrole, and reaction time, on the properties of the poly(vinyl alcohol)–PPy film. Kise *et al.*[11,12] investigated the properties of polyurethane–PPy foam by vapour-phase polymerization and correlated the effects of temperature, types and concentration of oxidants, and time of polymerization on the conductive properties of the composite foam.

In this work, we would like to report a systematic study of the vapour-phase chemical polymerization process of pyrrole using $FeCl_3$ as the oxidant. We would like to explore the possibility of using cotton thread, another kind of cellulose material that is widely available, as the support for the PPy under vapour-phase chemical polymerization. Moreover, the cotton thread has a well defined dimension, which is easily fabricated into various fixed lengths compared to using cotton fabric or filter paper, which would involve a more laborious fabrication process. We investigated the effects of the following factors, i.e. solvents, reaction time,

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*To whom correspondence should be addressed pyrrole and oxidant concentrations, and temperature, on the process of vapour-phase chemical polymerization of pyrrole, which would determine the final resistance of the PPy supported on the cotton thread (PPy/thread). We used the final resistance of the PPy for the characterization of the vapour-phase polymerization process.

EXPERIMENTAL

Pyrrole monomer (Aldrich) was redistilled and stored in a freezer maintained at −10°C. Ferric chloride (anhydrous) (BDH) was used without any further purification. Ferric chloride solutions were prepared in methanol. A 100% white cotton thread of diameter approximately 0.3 ± 0.05 mm and length ca. 40 mm was used as a substrate. The solvents employed, namely toluene, n-hexane, methanol and acetone, were reagent grade and used without any further purification.

The PPy/thread was fabricated using the following procedure: The cotton thread of about 40 mm was placed on top of a ruler. A fixed volume of $FeCl_3$ (0.2 μl) was spotted at a distance of 12 mm from one end of the thread via a fine glass capillary, diameter about 100 μm. The volume of the capillary was calibrated by weighing water in the capillary and a fixed mark was made on the glass capillary to ensure that the volume of $FeCl_3$ solution introduced on each cotton thread was equal. The $FeCl_3$ solution would spread to a distance of approximately 6 mm on both sides of the spot by capillary action and methanol was evaporated in air before polymerization. This thread was introduced into a glass bottle (volume ca. 50 ml) presaturated with 0.5 ml of pyrrole monomer solution to allow vapour-phase polymerization to occur. Timing began once the thread was placed in the capped glass bottle.

The resistance of the PPy/thread was measured with Hewlett-Packard HP 3466A digital multimeter using a four-point probe as shown in *Figure 1*. The PPy/thread was pressed by four pieces of graphite glued to a glass support, with a channel width of 1.5 ± 0.05 mm. The PPy/thread was introduced from one end, pressed gently by the four graphite pieces in order to connect the channel. A strong paper clip was used to hold the PPy/thread placed between the four graphite pieces prior to measurement to ensure good contact. The ends of the graphite were connected by crocodile clips to the multimeter. The resistance was measured once the polymerization was completed.

RESULTS AND DISCUSSION

In the chemically oxidative polymerization of pyrrole, the types and concentrations of oxidants, the kinds of solvents, reaction time and temperature, and the ratio of oxidant to pyrrole monomer play an interactive role in determining the physical and chemical properties of the PPy/thread. The present chemical oxidative system occurs under the vapour state and is limited by the concentration of $FeCl_3$ oxidant.

During the fabrication process, it was observed that $FeCl_3$ (methanol) solution moved along the cotton thread by capillary action whereas an aqueous solution of $FeCl_3$ was difficult to spot on the cotton thread and also water evaporation was slow. Therefore, methanol was used as the solvent for dissolving $FeCl_3$ throughout this work.

There was a concentration gradient of $FeCl_3$ solution along the cotton thread, with the maximum concentration located at the spot where $FeCl_3$ was initially spotted. Thus, the final resistance varied along the length of the thread. A consistent procedure was adopted to ensure that the resistance was always being measured at the same spot for each PPy/thread. The part of the PPy/thread formed with the maximum $FeCl_3$ concentration was always placed in the middle of the channel formed by the graphite pieces.

We investigated the reproducibility of the 'home-made' four-point probe for the resistance measurement (*Figure 1*). *Table 1* shows the reproducibility of measurement using the four-point probe for one PPy/thread under a set of typical experimental conditions. *Table 2* shows the results of the reproducibility of the fabrication of six PPy/threads formed under the same conditions. It indicated that the measurement could cause 5.6% deviation; however, this was less than the deviation of 6.1% that resulted from PPy/thread fabrication.

Figure 2 shows the variation of the resistance of PPy/thread with respect to the polymerization time for pure pyrrole vapour for 1 M $FeCl_3$ at the temperature of 25°C. The resistance decreased steeply within the first 20 s and became stable after 2 min. The thickness of the PPy coating increased with time, as depicted by the change of colour of the cotton thread. Initially, the thread was yellow (colour of $FeCl_3$) and then quickly covered with black PPy during the course of polymerization. The

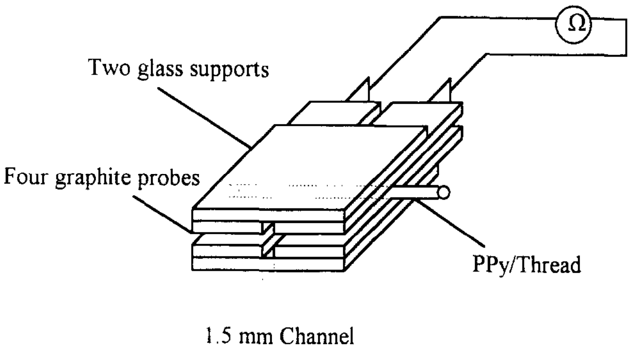

Figure 1 Diagram of a four-point probe for resistance measurement

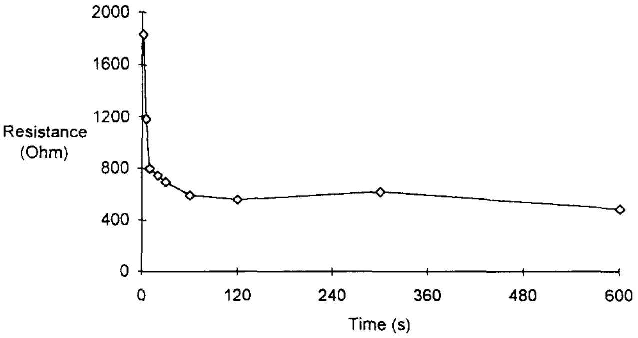

Figure 2 Time dependence of vapour polymerization when 0.2 μl of 1 M $FeCl_3$ was coated on a thread and exposed to pure pyrrole vapour at 25°C

Table 1 Results of the resistance for a PPy/thread[a]

Measurement No.	1	2	3	4	5
Resistance (Ω)	498	446	493	500	457

[a] Experimental conditions: concentration of $FeCl_3$ = 1 M, polymerization time = 10 min, temperature = 25°C, pure pyrrole monomer vapour. $\bar{x} = 479\,\Omega$, $\sigma(n-1) = 27\,\Omega$

Table 2 Results of the resistance for different Ppy/threads[a]

Thread No.	1	2	3	4	5	5
Resistance (Ω)	495	460	512	476	504	570

[a] Experimetnal conditions: concentration of $FeCl_3$ = 1 M, polymerization time = 10 min, temperature = 25°C, pure pyrrole monomer vapour. $\bar{x} = 503\,\Omega$, $\sigma(n-1) = 31\,\Omega$

PPy/thread was greyish initially and became totally dark after 5 min. This indicated that the vapour-phase chemical polymerization is a fast process.

The resistance of PPy/thread increased with the decrease of the $FeCl_3$ concentration (*Figure 3*). However, this increase was not linear: the resistance increased sharply at low $FeCl_3$ concentrations. Such a phenomenon was also reported for a PPy–poly(vinyl alcohol) composite film prepared by chemical vapour polymerization in which the conductivity was saturated when the $FeCl_3$ concentration was about 1.2 M (ref. 9). The thickness of the PPy formed increased with increasing concentration of $FeCl_3$, as depicted by the change of the colour from greyish to a totally dark PPy/thread.

The effect of temperature on the formation of PPy/thread was greater when the temperature was below 25°C (*Figure 4*). When the temperature was low, there could be two possible causes for the high resistance of the PPy. First, the vapour pressure of pyrrole was low at lower temperature, which reduced the pyrrole concentration in the vapour phase, so that less PPy was produced. Secondly, the diffusion of the pyrrole vapour to the $FeCl_3$ was slow at low temperature. The slow diffusion rate could lead to the formation of PPy with a structure in favour of high resistance. This is in contrast to the general trend of chemical polymerization occurring in solution in which the conductivity of PPy is enhanced at lower temperature[16].

The effect of the concentration or vapour pressure of pyrrole (pyrrole mixed with water) on the polymerization is shown in *Figure 5*. It was clear that as the vapour pressure of pyrrole monomer decreased, the polymerization took a longer time to complete. For the case of pure and 10% (v/v pyrrole/water), the resistance became stable within 30 s. When the pyrrole concentration was 1 and 0.5%, the resistance took minutes to stabilize. This is expected due to the lower vapour pressure of pyrrole. The final resistance of the PPy formed was not critically dependent on the vapour pressure of the pyrrole monomer since the polymerization was limited by the concentration of $FeCl_3$. It was found that the PPy that was formed in the presence of water vapour gave a more stable reading compared to the PPy formed under pure pyrrole vapour.

Figure 6 shows the solvent effect on the polymerization with 1 M $FeCl_3$ solution at 25°C, in which the pyrrole

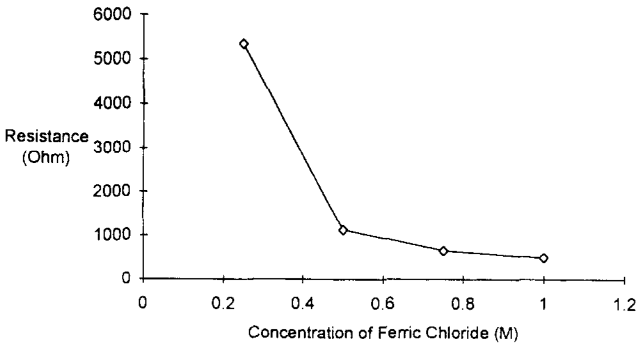

Figure 3 Effect of concentration of $FeCl_3$ oxidant on vapour polymerization when 0.2 μl of $FeCl_3$ with various concentrations was coated on a thread and exposed to pure pyrrole vapour at 25°C

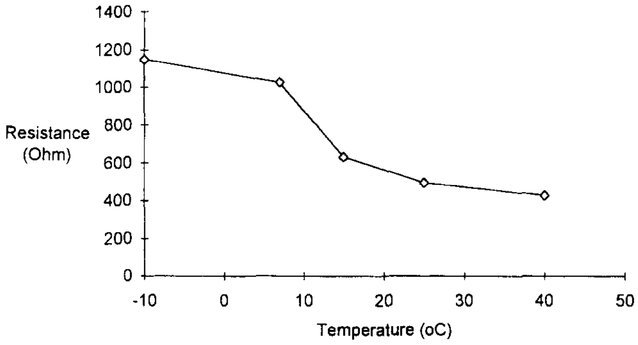

Figure 4 Effect of temperature on vapour polymerization when 0.2 μl of 1 M $FeCl_3$ was coated on a thread and exposed to pure pyrrole vapour at various temperatures

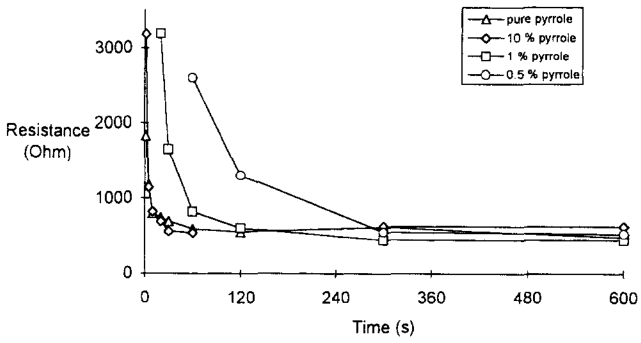

Figure 5 Effect of vapour pressure of pyrrole on vapour polymerization when 0.2 μl of 1 M $FeCl_3$ was coated on a thread and exposed to different head spaces at 25°C

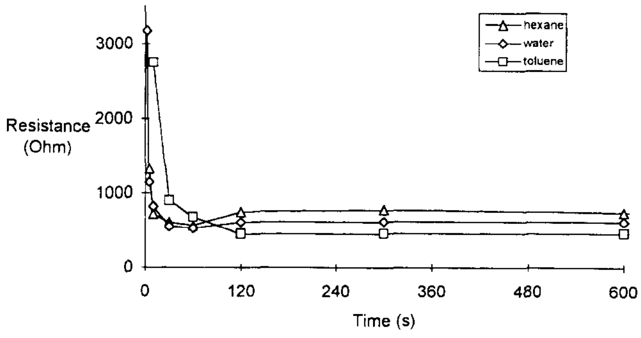

Figure 6 Effect of solution on vapour polymerization when 0.2 μl of 1 M $FeCl_3$ was coated on a thread and exposed to pyrrole solutions at 25°C

concentration was 10% with respect to other solvents employed, namely water, hexane and toluene. The polymerization rate generally showed a similar trend, i.e. the resistance of the PPy decreased steeply during the initial state of polymerization and stabilized quickly. Water and hexane showed very similar behaviour in which the resistance was stabilized within the first minute whereas toluene took a longer time to stabilize, about 2 min. Nevertheless, the final resistance of the PPy was independent of the solvent. Extensive work has been done on the solvent effect of the chemical polymerization of PPy in solution[1,3]. The conductivities of the PPy in hexane and water differ by one order of magnitude[3], under the same $FeCl_3$ concentration. But in our work on vapour polymerization for hexane and water systems, the final resistance did not differ substantially.

We attempted to employ acetone and methanol as one possible solvent. But we could not obtain any polymer and the $FeCl_3$ spread to the whole length of the cotton thread because $FeCl_3$ is soluble in acetone and methanol. Acetone and methanol have higher vapour pressure (125 and 230 mmHg at 25°C respectively according to the Antoine equation[17]), so that these solvents reduce the concentration of $FeCl_3$ along the cotton thread drastically. Even though $FeCl_3$ is soluble in water, the relatively low vapour pressure of water (23.8 mmHg at 25°C (ref. 17)) did not alter its concentration. $FeCl_3$ has very low solubility in hexane or toluene. Thus, they are good solvent system for the vapour-phase polymerization of pyrrole.

CONCLUSIONS

PPy was formed via vapour-phase chemical polymerization on a cotton thread that was coated with $FeCl_3$ and exposed to a head space with pyrrole vapour. The electrical resistance of this conductive polypyrrole thread was measured using a specially designed four-point probe. The effects of the concentrations of the oxidant $FeCl_3$ and pyrrole monomer, temperature, solvent and polymerization time on the resistance of PPy/thread formed by vapour-phase polymerization were investigated. The polymerization process was fast, and can be completed within seconds. Increasing concentration of $FeCl_3$ reduced the resistance of the film; the upper limit of the concentration to be effective was about 1.2 M. The resistance was higher for the polymer formed at lower temperature. Solvents such as hexane, toluene and water could be employed for this process but methanol and acetone could not be used. The suitability of each solvent was dependent on its vapour pressure and the solubility of $FeCl_3$ in the solvent.

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