Transparent, Electrically Conductive Composites Derived from Polypyrrole and Poly[Vinyl Chloride) by Vapor-Phase Polymerization: Effect of Environment on Polymerization and Reaction Mechanism

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PLEASE SCROLL DOWN FOR ARTICLE

TRANSPARENT, ELECTRICALLY CONDUCTIVE COMPOSITES DERIVED FROM POLYPYRROLE AND POLY(VINYL CHLORIDE) BY VAPOR-PHASE POLYMERIZATION: EFFECT OF ENVIRONMENT ON POLYMERIZATION AND REACTION MECHANISM

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ABSTRACT

Transparent, electrically conductive composite films were obtained by vapor-phase polymerization of pyrrole into a poly(vinyl chloride)(PVC) matrix containing $FeCl_3$. The effects of water and of organic solvents on the polymerization were investigated. It was found that the conductance of the films increases in the presence of both water vapor and of good solvents or swelling agents for PVC. The conductivity of the films rises with reaction time and so does the rate of increase with higher $FeCl_3$ concentration. The production of HCl was monitored by two methods, the precipitation of AgCl in an aqueous solution of silver nitrate and the increase in conductance of an aliquot of distilled water which had been placed into the reaction chamber. On the basis of our experimental results, we propose a reaction mechanism that explains the observed increase of conductance with time. A universal kinetic formula has been

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derived which relates the increase of electrical conductance to other parameters characterizing the boundary conditions of the polymerization.

1. INTRODUCTION

There has been a continuing interest in electrically conductive organic polymer films [1]. Most of the work in this area can be classified into three main classes, namely into studies on polyacetylene (PA) and its derivatives [2], poly(p-phenylene) (PPP) and its derivatives [3-5], poly(heterocyclic cations) [6-8], and polyaniline (PAn) [9]. The interest in polyacetylenes stems from their high electrical conductivity. Unfortunately, the intrinsic mechanical properties of PA are degraded by chemical doping processes, making it brittle. Furthermore, the doped PA has been described mostly as a material of very poor stability under ambient conditions, as is common for unsaturated polymer chains. But recently there have been reports of PA with a new, modified morphology that is more resistant.

The conductivity of PPP doped with AsF_5 may become comparable to that of PA. However, PPP is mostly obtained in the form of a black powder.

Poly(heterocyclic cations) such as polypyrrole (PPy) [7] and polythiophene (PTh) [8], on the other hand, show high electrical conductivity associated with high stability when exposed to ambient conditions. The drawbacks of these polymers are their poor mechanical properties, as indicated by their low elongation at break and their brittleness.

To improve the mechanical properties of conductive polymers, several approaches have been taken. Electrically conductive composites composed of PA and low-density polyethylene (LDPE) have been prepared by impregnating LDPE films with a Ziegler-Natta catalyst and exposing them to acetylene. Furthermore, the physical properties of block-type copolymers consisting of acetylene and styrene or isoprene have also been reported [10]. Composites derived from PPy and PVC by electropolymerization have also been studied [11]. Recently, the vapor-phase polymerization of a composite film derived from poly(vinyl alcohol) and PPy has been reported, which resulted in a transparent, conductive organic film [12]. The chemical synthesis of other conducting composites has also been reported [13].

In this paper we present the effects of different boundary conditions during vapor-phase polymerization on the conductance of the composite film derived from PVC and PPy. Special attention was devoted to the changes caused by the simultaneous presence of the vapors of selected solvents or by

changing the temperature. Based on these data, we propose a reaction mechanism for the formation of electrically conductive composites which can explain the observed increase in conductance with time.

2. EXPERIMENTAL

2.1. Preparation of the Composite Films

$FeCl_3 \cdot 6H_2O$ was dissolved in tetrahydrofuran (THF) to which PVC was added. The weight ratios of $FeCl_3 \cdot 6H_2O$ to PVC ranged between 0.5 and 1.75. The materials were spin-coated onto glass substrates at 900 rpm. The film thickness was measured with a Sloan Dektak profilometer. Free-standing polymer films were obtained by peeling them off from the substrate. The PVC films containing $FeCl_3$ were exposed to pyrrole (Janssen Chemica, used as received) vapor in a 1-L capped reaction vessel. Six films of various $FeCl_3$ concentrations were attached to the inside wall of the reaction vessel.

To investigate the effects of the added gases on the conductance of the resulting composite films, the reaction vessel was purged with the respective gases (Ar, N_2, or O_2) after the films had been attached. In order to investigate the effect of temperature on the polymerization, the reaction vessel was maintained in a refrigerator or in an oven. The temperature for each condition was monitored.

2.2. Measurement of Electrical Resistance of the Composite Films

The electrical resistance of the films was measured by the four-probe technique with a Wayne Kerr Multi Bridge 6425 in ambient air. The advantage of this method is that it allows the contact resistances to be neglected. The contact head consisted of four needles with a diameter of 0.5 mm each. The space between the needles was 7 mm. Due to the known difficulties in measuring the electrical resistance of such films [14], the directly measured values of the corresponding conductances are given in the figures. In calculating the specific conductivity from these data, 1 mS corresponds to 14 S/cm if the film thickness is considered to be 10 μm, the length 7 mm, and the width 0.5 mm, as determined by the diameter of the needles.

The measurements were carried out at ten different places for each film. Both the lowest and the highest values are included in the following figures.

In order to measure the time-dependent change of the conductance during polymerization, the voltage drop across a constant resistor of 3 kΩ in series with the film was monitored; a constant-voltage supply of 5 V (Volt-

craft DC power supply) was used. This assured that the films maintained contact to two separate cylindrical electrodes.

3. RESULTS AND DISCUSSION

3.1. Relation between Reaction Time and Film Conductance

The values measured for the electrical conductance of the composite films are shown in Fig. 1 as a function of reaction time, i.e., as a function of exposure time of the $FeCl_3$-PVC films to the pyrrole vapor, so that $FeCl_3$ concentration served as a variable (Fig. 1). The polymerization reaction was conducted in ambient air. Although there is some scatter among the observed values, we conclude from Fig. 1 that the conductance of the composite film increases with reaction time. It is also noted that the time to reach the saturation value of the conductance is shorter for higher than for lower $FeCl_3$ concentrations.
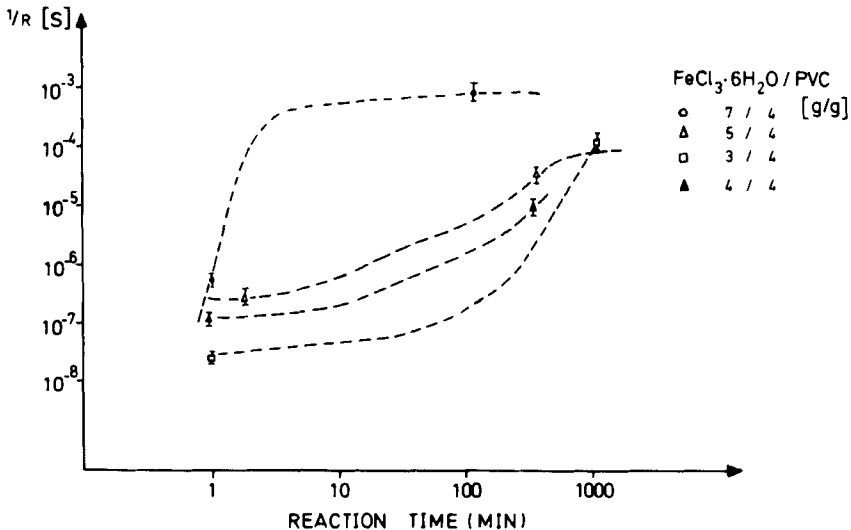

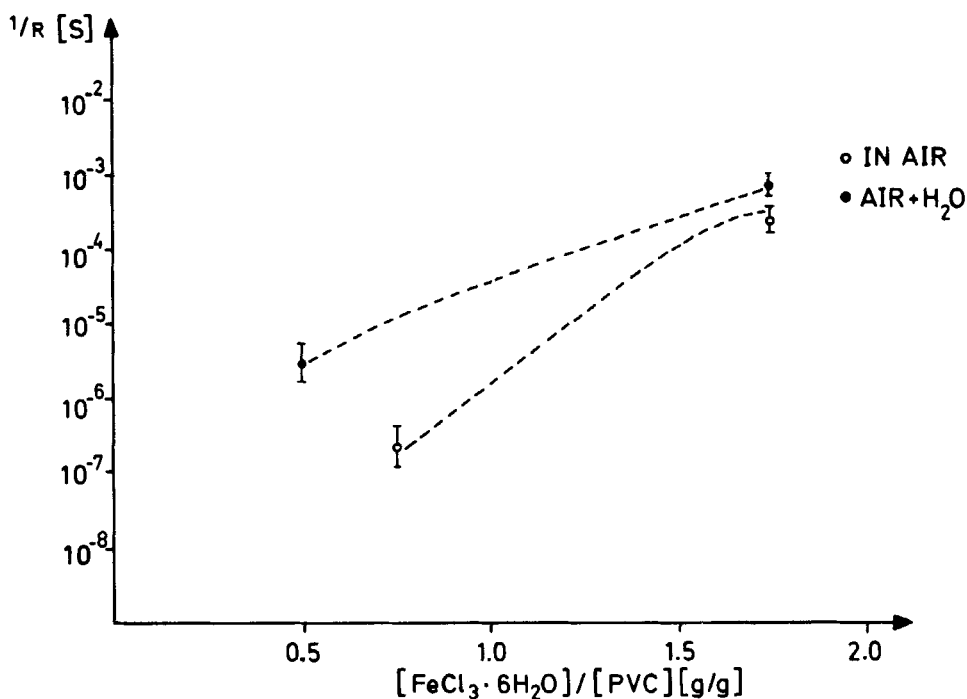FIG. 1. Dependence of conductivity on reaction time.

FIG. 2. Influence of water on the conductivity. Reaction time: 2 h.

3.2. Effects of Boundary Conditions

The conductance of the composite films obtained in argon, nitrogen, oxygen, and air environment was studied for different $FeCl_3$ concentrations. The reaction time was standardized at 2 h. It was found that the conductance values of the composite films obtained in the gas-purged environment are lower than those obtained in ambient air.

To investigate the effect of humidity on the conductance of the composite films, the polymerization was also carried out under air saturated with water vapor. The results of experiments conducted in the presence of 10 mL water in the reaction vessel (Fig. 2) show that the conductance of samples polymerized under water vapor is higher than that obtained in ambient air. This fact was also confirmed in a nitrogen-purged environment. Consequently, the reproducibility of the conductance values will be affected by the day-to-day change in the ambient humidity unless proper precautions are taken.

$^{1}/_{R}$ [S]

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10⁻²
10⁻³                                                    • WITH  THF
10⁻⁴                                                    ▲ WITH ⬡-O
10⁻⁵                                                    ····WITH CH₃CN
10⁻⁶                                                    --WITH MeOH
10⁻⁷
10⁻⁸

        0.5        1.0        1.5        2.0
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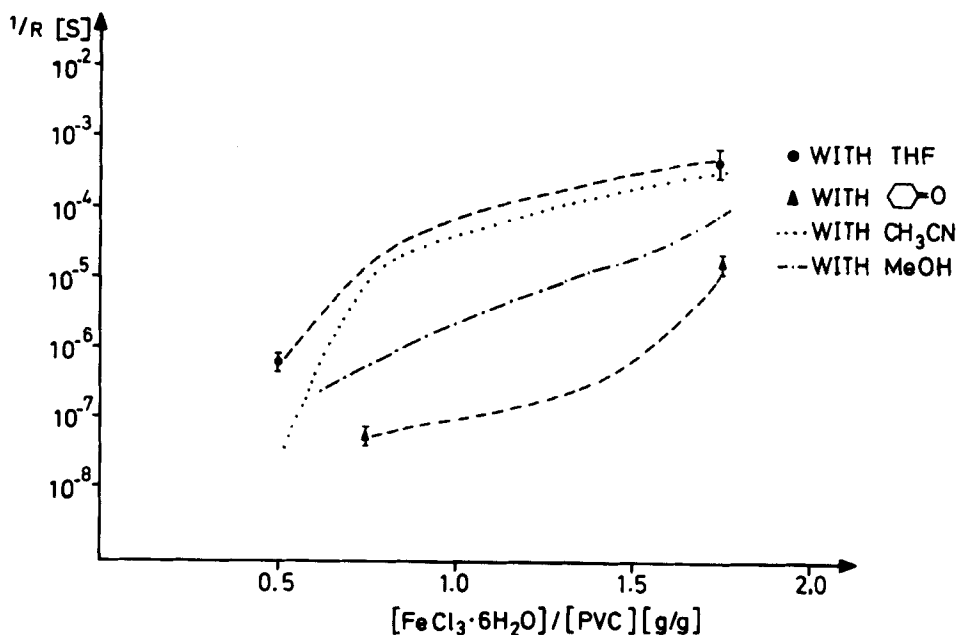
$[FeCl_3 \cdot 6H_2O] / [PVC] [g/g]$

FIG. 3. Dependence of the conductance on the solvent.

The conductance of the composite films obtained in the presence of various solvent vapors is shown in Fig. 3. Standard reaction time was again 2 h. It is apparent that the presence of some solvents, e.g., THF, DMF, dioxane, or acetonitrile, results in higher conductance of the films. On the other hand, the presence of methanol or cyclohexanone fails to show the increase in the film conductance. All solvents which increase the conductance can be classified as good solvents or swelling agents for PVC. The role of cyclohexanone is not yet clear because it is a good solvent for PVC but does not increase the conductivity of the composite. It is possible that a complex of $FeCl_3$ and cyclohexanone might be formed, which could preclude the polymerization of pyrrole and/or its doping.

One possible explanation for the observed increase in the conductance of the composite films polymerized in the presence of organic solvents might be that the organic vapor swells the PVC, which then promotes the mobility of the $FeCl_3$ in the PVC films. This would result in an increase of the reaction probability of both polymerization and doping.
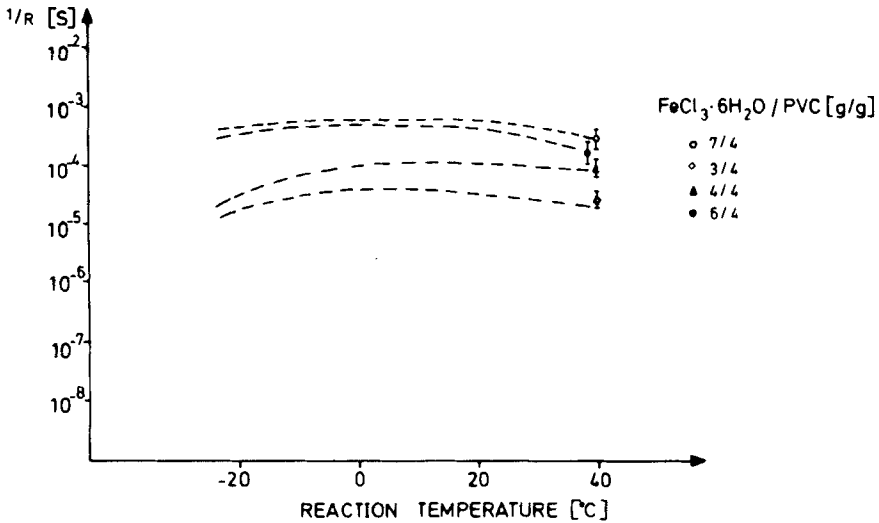
FIG. 4. Relationship between reaction temperature and conductivity. Reaction time: 2 h.

Among the organic solvents examined here, THF gives the best conductance values for a 2-h reaction period.

3.3. Effect of Reaction Temperature

The dependence of film conductance on reaction temperature is shown in Fig. 4. Within the temperature range studied here (-24 to 40°C), no significant difference is observed. Although a slight decrease in conductance is found when the polymerization is carried out at lower temperature (-24°C), it is considered to be more important that composite films polymerized at this lower temperature are more transparent than those made at room temperature. Therefore, in order to obtain good optically transparent conductive films, polymerization at lower temperature might be crucial, as demonstrated in a previous report [12].

Obviously, an increase in the reaction temperature results in an increase of the pyrrole vapor pressure and thus in the reaction rates. The rate of polymerization is also expected to increase with increasing reaction temperature. It is conceivable that, if the reaction is carried out at higher temperatures, the con-
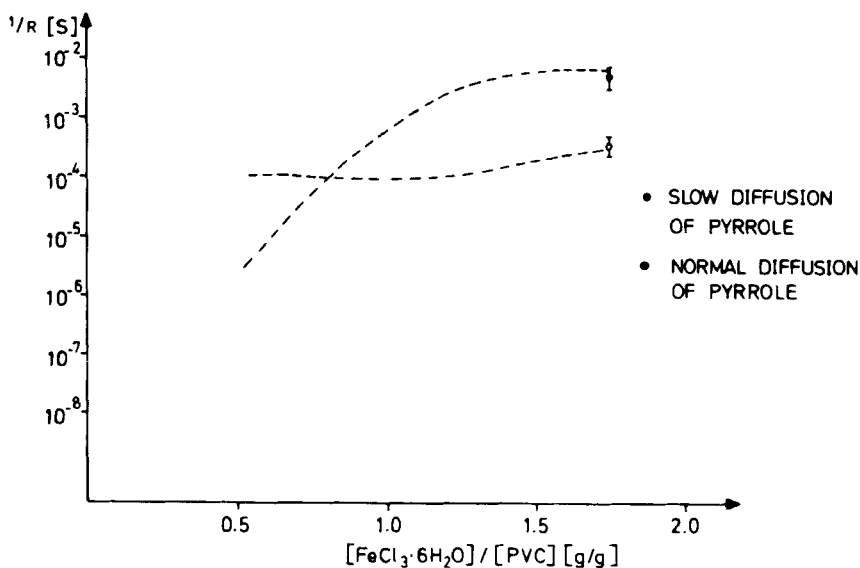
FIG. 5. Influence of the diffusion rate of pyrrole vapor on the conductance. Reaction time: 15 h.

sumption of $FeCl_3$ is higher due to a higher polymerization rate, and not enough $FeCl_3$ will be left behind for doping the resulting polymer.

If the rate of diffusion of pyrrole vapor into the reaction vessel is restricted by putting the $FeCl_3$-PVC precomposite into a vessel covered with a lid containing a small hole, the influence of the availability of pyrrole vapor on the conductance of the resulting films can be monitored. As shown in Fig. 5, the conductance of films polymerized under pyrrole vapor supplied through a small hole is higher for higher initial $FeCl_3$ concentrations than for those obtained in an otherwise identical experiment in which pyrrole vapor was provided freely without a restricting hole. The conductance of the resulting composite films is not only determined by the content of PPy in the films, but also by the degree of doping.

3.4. Other Monomers

The conductance of a $FeCl_3$-PVC film shows no increase when the sample is exposed to the vapor of other oxidizable monomers, as presented in Fig. 6.
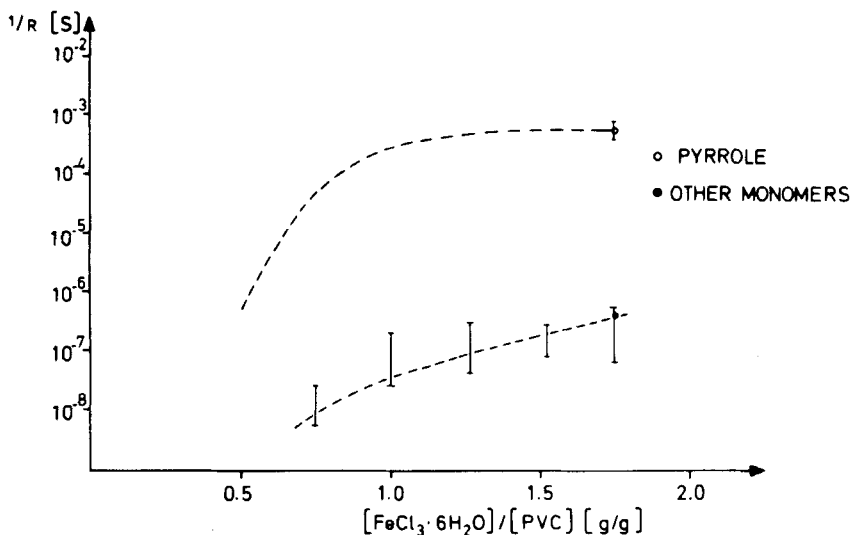
FIG. 6. Effect of different monomers.

This finding seems to be due to the fact that the oxidation potentials of the other monomers are higher than that of pyrrole (except for N-methylpyrrole) [15]. N-Methylpyrrole seems to polymerize in the $FeCl_3$-PVC precomposite since a color change of the film is observed. However, either the content of the resulting polymer and/or the degree of its doping seems to remain low in addition to its known low intrinsic conductivity [15]. Accordingly, only pyrrole has been found to result in a sufficient increase in film conductance under these vapor-phase polymerization conditions.

3.5. Detection of HCl Production

Production of HCl during the vapor-phase polymerization of pyrrole was confirmed by two methods. (1) When an aqueous silver nitrate solution was placed in the reaction vessel, a white precipitate formed in the solution. (2) In addition, the increase in conductance of an aliquot of distilled water placed in the reaction vessel was monitored (Table 1). It is assumed that this increase of conductivity is due to the dissolution in the water of HCl generated by the polymerization reaction. No increase of the conductivity of the distilled water was observed when only $FeCl_3$-PVC films were placed in the reaction vessel or when only pyrrole or THF was present.

TABLE 1. Increase of Conductivity in Distilled Water during Polymerization

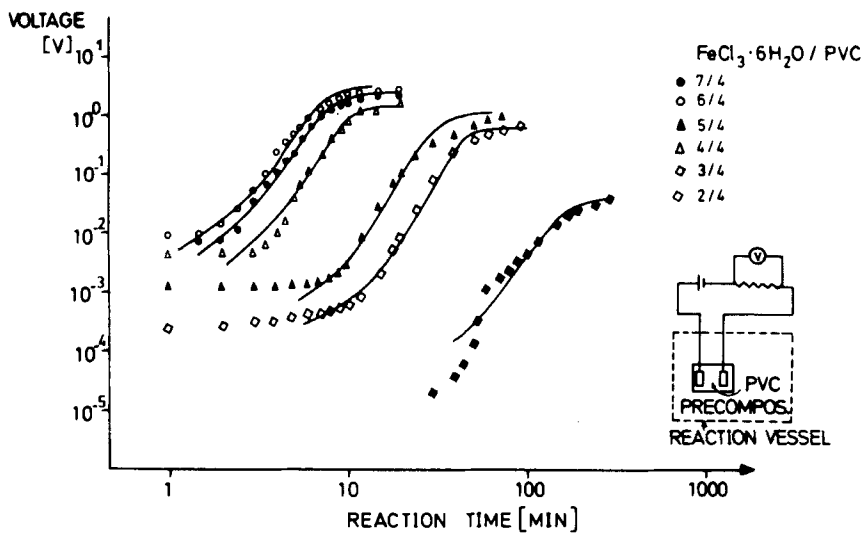| Time, t, min	Output, mV
10	10.06
20	19.94
30	28.74
40	35.80
50	40.07
60	45.50
70	49.02
80	52.20

FIG. 7. Measured (points) and calculated (curves) change of conductance with reaction time.

3.6. Reaction Mechanism

The effect of the concentration of $FeCl_3$ in the precomposite on the electrical conductance of the films in the presence of THF vapor was measured as a function of reaction time. Again, the trend of the increase in conductance is similar to that observed in the absence of THF vapor (Fig. 1) although the time to reach the saturation conductance is shorter than in the absence of THF vapor. The changes in the film conductance during the early stages of reaction are difficult to measure by the four-probe method because of the rapid increase in conductance. Therefore, the onset of conduction was monitored by measuring the voltage drop across a constant resistor placed in series with the $FeCl_3$ film, as shown in Fig. 7.

Based on the experimental results detailed above, we propose the reaction mechanism outlined in Scheme 1. As reported in a previous paper on electropolymerization [15], the pyrrole cation radical, which is an intermediate during the oxidation reaction, plays an important role in the polymerization. Accordingly, the protons produced by the polymerization reaction combine with the Cl^- resulting from the $FeCl_3$ reduction, yielding HCl. As has been
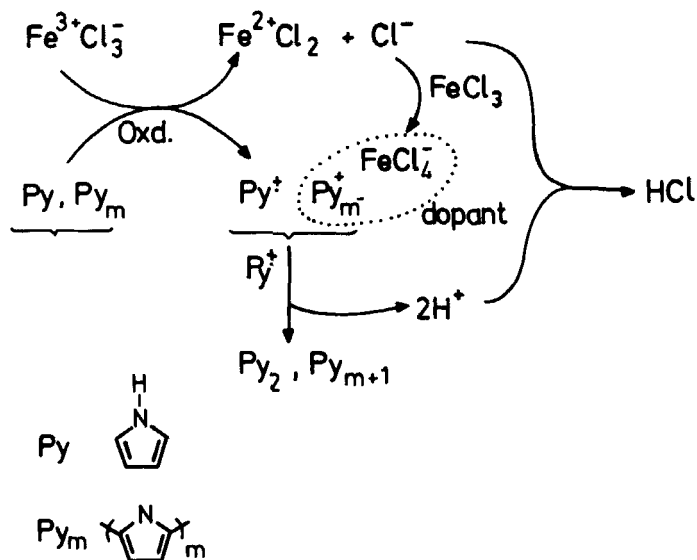
SCHEME 1. Reaction mechanism.

previously reported in a study of the chemical doping of PA [16] and of PPy [17], $FeCl_4^-$ can be considered to be the counterion for the PPy cation in our case as well.

Based on the reaction mechanism given in Scheme 1, the decrease in Fe^{3+} concentration with time can be expressed by the equation

$$\frac{d[Fe^{3+}]}{dt} = -k_0[Fe^{3+}][Py] - k_{01}[Fe^{3+}]\{[Py_2] + [Py_3] + \cdots + [Py_n]\}$$

$$- k_{02}[Fe^{3+}]\{[Py_2^+] + \cdots + [Py_n^+] + \cdots + [Py_n^{2+}] + \cdots$$

$$+ [Py_n^{3+}] + \cdots\}, \tag{1}$$

where k_0 is the rate constant for the oxidation of the pyrrole (Py) monomer, k_{01} is the rate constant for oxidation of the pyrrole oligomers and the polymer, k_{02} is the rate constant for the oxidation of both the cations of the oligomer and of the polymer, [Py] is the concentration of the pyrrole monomer, Py_2 refers to the dimer of pyrrole, and similarly Py_n refers to the n-mer. The first term on the right-hand side of Eq. (1) corresponds to the oxidation rate of the pyrrole monomer, the second term to the oxidation rate of the pyrrole oligomer and the polymer, and the third term to the oxidation rate of the cations of the pyrrole oligomer and of the polymer cations. The oxidation reaction of the oligomer, the polymer, and their cations includes the doping reaction. If we assume that the PPy in a composite film has the most probable distribution [19], the total concentration (C_t) of the oligomers and of the polymer can be described by

$$C_t = [M_2] + [M_3] + \cdots + [M_n]$$

$$= [M_2](1 + r + r^2 + \cdots + r^{n-2}) \tag{2}$$

$$= [M_2] \, 1/(1 - r),$$

where r is the fraction of the monomers which has reacted with the monomer. If the doping reaction proceeds in synchronism with the polymerization and the doping level is q, the total concentration of the oligomer and polymer cations can be expressed by

$$[M_2^+] + [M_3^+] + \cdots [M_n^+] + \cdots + [M_2^{2+}] + \cdots + [M_n^{2+}] + \cdots$$

$$+ [M_n^{3+}] + \cdots = [M_2](2 - r)/(1 - r)^2 q \tag{3}$$

because the total number of pyrrole monomer units in the polymer can be calculated by the relation

$$2[M_2] + 3[M_3] + 4[M_4] + \cdots + n[M_n]$$

$$= [M_2]\{2 + 3r + 4r^2 + \cdots + nr^{n-2}\} \tag{4}$$

$$= [M_2](1/r)\{\Sigma\, nr^{n-1} - 1\}.$$

The $FeCl_3$ concentration consumed in polymerization at time t is given by

$$2[M_2] + 4[M_3] + 6[M_4] + \cdots + 2(n-1)[M_n]$$

$$= 2[M_2](1 + 2r + 3r + \cdots + (n-1)r^{n-2}) \tag{5}$$

$$= 2[M_2]\{1/(1-r)^2\}.$$

If the fraction of Fe^{3+} consumed at time t is p, the Fe^{3+} concentration at t can be expressed by

$$[Fe^{3+}(t)] = c_0(1 - p), \tag{6}$$

where c_0 is the initial Fe^{3+} concentration.

Since $c_0 p$ ($= [Fe^{3+}]$ consumed at t) is equal to (Fe^{3+} concentration consumed for the pyrrole polymerization) plus (Fe^{3+} concentration consumed by the doping), the sum of Eqs. (3) and (5) represents $c_0 p$:

$$c_0 p = 2[M_2] + [M_2]\,2(2 - r)/(1 - r)^2 q. \tag{7}$$

The factor 2 in the second term of this equation is due to the consumption of an additional $FeCl_3$ for doping (assuming the counterion is $FeCl_4^-$, see Scheme 1). Equation (7) can thus be rewritten as

$$[M_2] = c_0 p/2k, \tag{8}$$

where $k = \{1 + (2 - r)q\}/(1 - r)^2$. Substituting Eq. (8) into Eqs. (2) and (3), one obtains

$$[M_2]\frac{1}{(1-r)} = \frac{c_0 p}{2k(1-r)} \tag{2'}$$

$$[M_2] \frac{(2-r)}{(1-r)2q} = c_0 p \frac{(2-r)q}{2k(1-r)2} . \tag{3'}$$

Substituting Eq. (2') and Eq. (3') into Eq. (1), one obtains the expression for p from

$$-dp/dt = -(1-p)(a+bp), \tag{9}$$

where $a = k_0 [M]$ and

$$b = k_{01}c_0/2k(1-r) + k_{02}c_0(2-r)q/2(1-r)^2 k.$$

Solving the differential Eq. (9), one obtains

$$p = \frac{1-e^{-at}}{1+De^{-at}}, \tag{10}$$

where $\alpha = a + b$ and $D = b/a$. If the conductance is proportional to the concentration of the cations of the oligomers and of the polymer, and if k and q are constant, the conductance turns out to be proportional to p. One then obtains the following expression for the current i:

$$i = Ap = A \frac{1-e^{-at}}{1+De^{-at}} . \tag{11}$$

The values of A, a, and D required to fit the experimental results of Fig. 7 are listed in Table 2.

Once the values of A, D, and α are selected, the current increase observed is fitted to Eq. (11) as shown by the solid lines in Fig. 7. It is surprising that the increase in current measured for different $FeCl_3$ concentrations can be explained by this universal equation even though the reaction mechanism is significantly simplified. However, α, i.e., the total oxidation rate for Py, its oligomers, and polymers, is not proportional to the $FeCl_3$ concentration for large D values, which in turn is the ratio of the oxidation rate of oligomer and polymer to that of Py monomer. Therefore, other factors such as an uneven distribution of $FeCl_3$ within the film might render the reaction on the PVC polymer surface more complex. In fact, a gradient of the $FeCl_3$ concentration in the PVC-$FeCl_3$ precomposite is expected to result from the spin-coating application of the films, and accordingly, differences in the

TABLE 2. Parameters Required to Fit Experimental Results to Eq. (11)

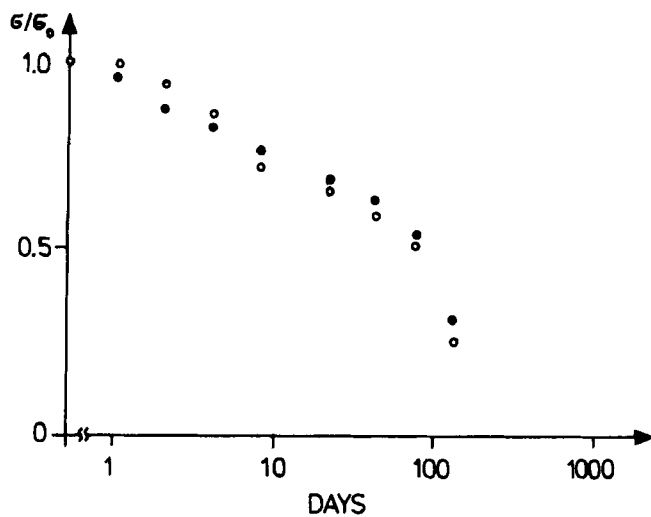| $FeCl_3 \cdot 6H_2O/PVC$, g/g	A, V	α, min^{-1}	D
7/4	3.0	1.1	1500
6/4	2.5	1.0	1500
5/4	1.6	0.8	2000
4/4	1.0	0.3	5000
3/4	0.69	0.2	5000
2/4	0.38	0.05	1000

FIG. 8. Stability of the conductance.

conductance were found between different locations on the surface of the film.

3.7. Stability of the Composite Films

The deterioration of the electrical conductivity in ambient air of the PVC-PPy composites obtained by vapor-phase polymerization is depicted in Fig. 8. Even though the drop in conductivity is considerable and unavoidable according to our current knowledge, the rate of deterioration is much lower than that of the composites made from LDPE and PA, as reported in the literature [18].

4. SUMMARY

Vapor-phase polymerization offers a method for preparing conducting composite films derived from PVC and PPy. The influence of boundary conditions on the properties of the films, in particular the conductance, is reported. A general equation for the increase of conductivity with increasing reaction time is established, based on the proposed reaction mechanism.

ACKNOWLEDGMENT

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