

Synthesis of Electrical Conductive Polypyrrole Films by Interphase Oxidative Polymerization—Effects of Polymerization Temperature and Oxidizing Agents

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ABSTRACT: Polypyrrole (PPy) films were synthesized by interphase polymerization reactions between aqueous solutions of oxidizer and organic solutions of pyrrole monomer. It was found that the conductivity and morphology of PPy films strongly depend on the diffusivity of pyrrole monomer into aqueous phase. It seems that polymerization should be carried out at lower temperatures in order to obtain homogeneous PPy films with high electrical conductivities. When PPy films were prepared with iron(III) chloride as an oxidant and toluene as an organic solvent, the conductivity increased from 2.7 to 9.7 S cm⁻¹ and film thickness decreased largely by changing reaction temperature from 10 to -5°C. The conductivity of PPy films was also dependent on the nature of oxidizing agent. The conductivities of PPy films obtained with iron compounds as oxidizing agents decreased in the order; perchlorate, chloride > nitrate > sulfate. The result may be attributed to the difference in extent of doping by counter anions. The maximum conductivity of PPy film prepared with iron(III) perchlorate was 32.6 S cm⁻¹.

KEY WORDS Polypyrrole / Interphase Polymerization / Oxidative Polymerization / Iron(III) Compound / Electrical Conductivity / Reaction Temperature / Anion Doping /

The conducting polymers consisting of five-membered heterocycles have attracted much attention from the viewpoint of both fundamental interest and potential applications.¹⁻⁴ Polypyrrole (PPy) has high antioxidative stability and is considered one of the most useful conducting polymers for practical applications. However, PPy is insoluble in any solvents and nonfusible even by heating up to the decomposition temperature; this has restricted processability and practical application of this polymer. PPy films have been prepared mainly by the electrochemical polymerization on the surface of electrodes.⁵⁻⁷ This method gave PPy films that have sufficiently good mechanical properties. The main drawback of this technique is that the

area of the film is restricted by the size of the electrode.

Chemical methods for oxidative polymerization of pyrrole have also been known for many years. Various oxidizing agents have been used including iron(III) chloride, which has been used most extensively.⁸⁻¹⁰ In order to overcome the difficulties in molding, techniques have been developed to prepare composite PPy films by polymerization of pyrrole in or on the surface of polymeric materials containing oxidizing agents.¹¹⁻¹³

Conductive PPy films were prepared by the interphase polymerization reactions between aqueous FeCl₃ solution and organic solutions of pyrrole. This method has an advantage of producing homogeneous PPy films of large

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area in simple reaction vessels.¹⁴ We reported recently that the morphology and electrical conductivity of PPy films prepared by this method were strongly affected by the nature of organic solvents and polymerization time. We also discussed the mechanism of the film growth on the basis of film properties and observation of the film surface by scanning electron microscope.¹⁵ This article reports the effects of polymerization temperature and oxidizing agents on the properties of PPy films. The importance of the diffusion of pyrrole monomer into aqueous phase and the nature of oxidizing agents will be discussed in terms of thickness and electrical conductivity of PPy films.

EXPERIMENTAL

Pyrrole monomer (Tokyo Kasei Kogyo Co.) was purified by distillation under reduced pressure. Anhydrous iron(III) chloride (Wako Pure Chemical Industries, Ltd.), iron(III) sulfate, iron(III) nitrate, iron(III) perchlorate, and the organic solvents (benzene, toluene, anisole, cyclohexane, *n*-pentane, *n*-hexane) (Nacalai Tesque Inc.) of guaranteed grade were used without further purification.

Before starting the reaction, an aqueous oxidant solution and a solution of pyrrole in an organic solvent were kept at the reaction temperature. The pyrrole solution was added gradually onto the oxidant solution placed in a glass vial. The two-phase reaction mixture was kept standing at a constant temperature. After the polymerization, the PPy films were washed by water and methanol and dried under vacuum for more than 24 h at 45°C.

Electrical conductivity of PPy films was measured by four probe method under vacuum at 30°C. UV-VIS spectra were measured by use of a Shimadzu UV-visible spectrophotometer UV-240. Scanning electron microscope (SEM) was performed using a Hitachi S-450 instrument.

RESULTS AND DISCUSSION

As described in the previous paper, when an organic solution of pyrrole was placed on an aqueous solution of iron(III) chloride, PPy film was formed and grew at the aqueous side of the interphase.¹⁵⁾ The growth rate and electrical conductivity of films were strongly dependent on the nature of the organic solvents, and this was assumed to be the consequence of the difference in the diffusion rates of pyrrole across the interphase. Therefore, we measured the distribution of pyrrole between aqueous and organic phases in order to elucidate the effect of the nature of organic solvents. Thus, an organic solution of pyrrole was added onto pure water, and after 4 h at 10°C, the concentration of pyrrole in aqueous phase was determined by taking UV spectra. The conductivity and film thickness of PPy films obtained using different organic solvents are listed Table I. Figure 1 shows the relation between the concentrations of diffused pyrrole in aqueous phase and thickness of PPy films which were obtained by the interphase polymerization under the same reaction conditions using corresponding organic solutions of pyrrole. There is a tendency that the film thickness increases with increase in the diffusivity of pyrrole into aqueous phase. Thick PPy films were bulky and porous as observed by SEM, which implies that these PPy films have low bulk densities because of rapid growth.

The above results suggested that reaction

Table I. Properties of solvents as organic phases and electrical conductivity and thickness of polypyrrole films

Solvent	Specific gravity	Conductivity Film thickness	
		S cm ⁻¹	μm
Benzene	0.8737	1—10	10
Toluene	0.8670	1—3	30
Anisole	0.9988	1—3	40
<i>n</i> -Pentane	0.6262	< 1.0	700
<i>n</i> -Hexane	0.6594	< 1.3	450

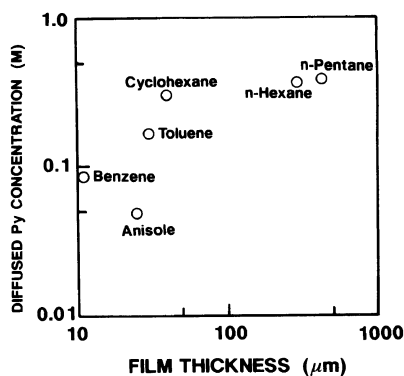


Figure 1. Relation between concentration of diffused pyrrole in aqueous phase and thickness of PPy films.

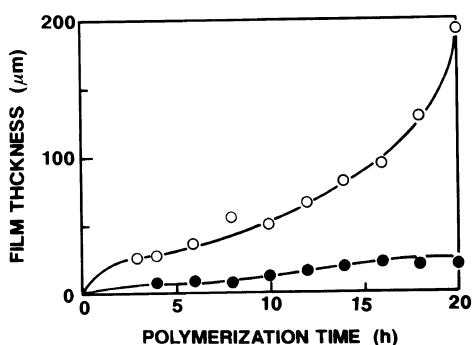


Figure 2. Changes in thickness of PPy films with polymerization time. Organic solvent, toluene; ○, 10°C; ●, -5°C; $[\text{FeCl}_3] = 2.4 \text{ M}$; $[\text{pyrrole}] = 1.3 \text{ M}$.

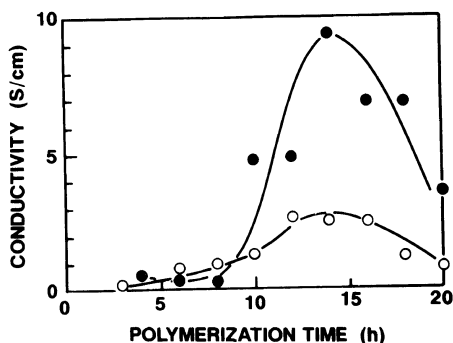


Figure 3. Changes in electrical conductivity of PPy films with polymerization time. Organic solvent, toluene; ○, 10°C; ●, -5°C; $[\text{FeCl}_3] = 2.4 \text{ M}$; $[\text{pyrrole}] = 1.3 \text{ M}$.

temperature might be also a controlling factor of the film structure and conductivity. It seemed that polymerization should be carried out at

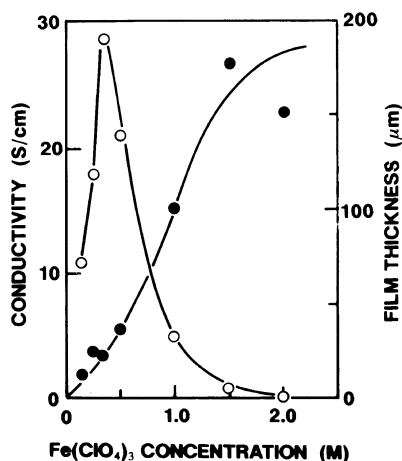


Figure 4. Changes in electrical conductivity and thickness of PPy films with $\text{Fe}(\text{ClO}_4)_3$ concentration. Organic solvent, benzene; ○, electrical conductivity; ●, film thickness; $[\text{pyrrole}] = 0.65 \text{ M}$, 10°C, 4 h.

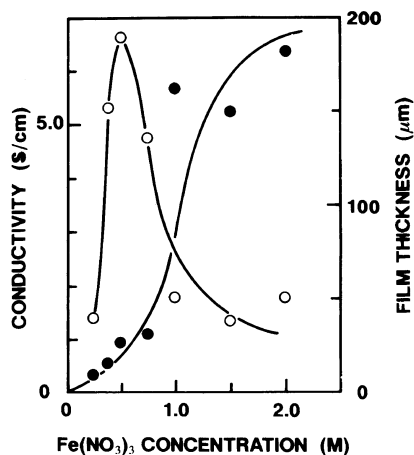


Figure 5. Changes in electrical conductivity and thickness of PPy films with $\text{Fe}(\text{NO}_3)_3$ concentration. Organic solvent, benzene; ○, electrical conductivity; ●, film thickness; $[\text{pyrrole}] = 0.65 \text{ M}$, 10°C, 4 h.

lower temperatures in order to obtain homogeneous PPy films with high electrical conductivity. Figures 2 and 3 show the thickness and electrical conductivity of PPy films prepared using toluene at 10 and -5°C, respectively. The film thickness decreased largely but maximum electrical conductivity increased from 2.7 to 9.7 S cm^{-1} by changing reaction temperature from 10 to -5°C. The

density of films obtained by 16 h reactions increased from 0.139 to 0.264 g cm⁻³ in going from 10 to -5°C. These results may be the consequence of lowering of reaction rate at -5°C due to slower diffusion of pyrrole into aqueous phase, so that PPy films with higher bulk densities were formed.

Figures 4–6 show the results of polymerization using different iron(III) salts (perchlorate, nitrate, and sulfate) as oxidizing agents at 10°C. As expected, both conductivity and thickness of PPy films are strongly dependent on the oxidant concentration. Thickness of PPy films increased with increasing oxidant concentration for all the reaction systems studied.

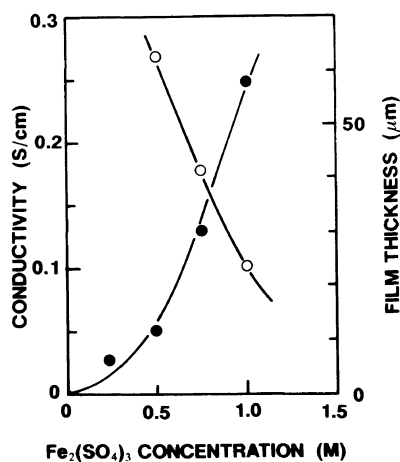


Figure 6. Changes in electrical conductivity and thickness of PPy films with Fe₂(SO₄)₃ concentration. Organic solvent, benzene; ○, electrical conductivity; ●, film thickness; [pyrrole] = 0.65 M, 10°C, 4 h.

However, when iron(III) perchlorate or nitrate were used, conductivity increased and then decreased sharply with the increase in oxidant concentration giving maximum conductivities of 28.4 and 6.6 S cm⁻¹ at around 0.4 M perchlorate and nitrate, respectively. A similar bell-shaped profile of conductivity with respect to oxidant concentration was reported for polymerization of pyrrole in methanol.¹⁰ The decrease in conductivity at higher oxidant concentrations may be explained by the decrease in film density as discussed above. Alternatively, excess amounts of the oxidant would lead to the loss of regularity in polymer structure; that is the decrease in the length of conjugation.

When pyrrole concentration was decreased from 0.65 M to 0.17 M, the conductivity increased up to 32.6 and 16.0 S cm⁻¹ using iron(III) perchlorate and nitrate, respectively. The conductivity of PPy films prepared with iron(III) sulfate decreased by increasing the oxidant concentration (Figure 6). In this case, PPy films prepared at lower oxidant concentrations were very thin, so that it was difficult to measure the conductivity.

The conductivities of PPy films obtained with iron compounds as oxidizing agents under the same reaction conditions decreased in the order; perchlorate, chloride > nitrate > sulfate. As described above, the conductivity is a function of film thickness, but, as Figures 4–6 show, significant differences are observed in the conductivities of films which have almost the

Table II. Atomic ratio of polypyrrole films (N = 1.00)^a

Oxidizing agent	Oxidizing agent concentration	Electrical conductivity	C	H	N	S	N	Cl
Fe ₂ (SO ₄) ₃	20 wt%	0.6 S cm ⁻¹	4.21	3.72	1.00	0.12		
Fe(NO ₃) ₃	15 wt%	5.7 S cm ⁻¹	4.00	3.20	1.00		0.24 ^b	
Fe(ClO ₄) ₃	17 wt%	14.9 S cm ⁻¹	4.05	3.51	1.00			0.32
FeCl ₃ ^c	2.4 M	11.1 S cm ⁻¹	4.14	4.03	1.00			0.32

^a [pyrrole] = 0.32 M; polymerization time = 4 h.

^b Calculated value of nitrogen in NO₃ ion by the assumption that the atomic ratio of carbon to nitrogen in PPy is 4.00.

^c [pyrrole] = 0.65 M.

same thickness but were obtained using different iron salts. The results of elemental analysis of the PPy films prepared with these oxidants are summarized in Table II. It is known that the conductivity of a conjugated polymer doped with an electron donor or acceptor is proportional to the third power of dopant concentration.^{16,17} Therefore, the difference in the conductivities of PPy films obtained with different oxidants may be due to difference in dopant concentrations as revealed by elemental analysis (Table II).

In conclusion, the present study indicates that the diffusivity of pyrrole from organic phase to aqueous phase is the primary factor to control the thickness and conductivity of PPy films prepared by interphase polymerization. Therefore, the nature of organic solvents and reaction temperature, as well as pyrrole concentration, have significant effects of film properties. The conductivity changes by the change in the density of the films. The conductivity of PPy films is also strongly dependent on the nature and concentration of oxidizing agents. It is assumed that the concentration of dopants derived from oxidants may be another factor which influences the conductivity of the PPy films.

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