Thin Polypyrrole Films Prepared by Chemical Oxidative Polymerization

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ABSTRACT: Polypyrrole (PPY) films with a thickness of $3-4 \ \mu\text{m}$ were obtained by chemical oxidation of pyrrole (PY) at the interface of chloroform and water with an oxidant $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The films were compact and could be removed with a solid plate. The quality and compositions of these films varied with the molar ratios of the monomer and oxidant of the reaction systems. Overoxidation of polypyrrole was observed and confirmed by the characterizations via infrared spectra and elemental analysis of the films. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2169–2172, 1998

Key words: polypyrrole; thin film; chemical oxidation; pyrrole

INTRODUCTION

The synthesis of heterocyclic conducting polymers has been investigated extensively in the last decades. One of them, polypyrrole (PPY), also has been widely studied since it presents a high electrical conductivity, interesting redox properties, and a satisfying environmental stability. Usually, thin films of PPY were obtained by electrochemical synthesis^{1,2} and powders (named as pyrrole black) by chemical oxidative polymerizations.^{3,4} Pyrrole (PY) black can be produced by homogeneous reactions of PY and various oxidizing agents, such as nitrous acid, lead dioxide, potassium persulfate, ferric chloride, quinone, diazonium salts, or ozone.^{5,6} In this article, we report a thin PPY film prepared by chemical oxidation of PY at the interface formed by a chloroform solution of pyrrole and an aqueous solution of $(NH_4)_2S_2O_8$.

EXPERIMENTAL

Materials

Pyrrole (Aldrich Chemical Co., Milwaukee, WI) was distilled before use. Dehydrated ammonium persulfate (analytical grade pure, Shanghai Aijian Chemical Factory, Shanghai, China) was used as received. Chloroform (Shanghai 1st Chemical Factory, Shanghai, China) was used after distillation.

Polymerization of PY

Polymerization of PY was performed by putting a 20-mL chloroform solution of pyrrole into each of four 100-mL beakers. The concentrations of PY were 2.0, 0.4, 0.2, and 0.1M. Then, a 20-mL aqueous solution of ammonium persulfate with a salt concentration of 0.2M was poured slowly on the chloroform solution within 10 s. An interface of chloroform and water appeared and became black

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Figure 1 SEM picture of the PPY film prepared from the system of $M_{\rm PY}/M_{\rm O} = 1$ and $M_{\rm O} = 0.2M$.

in every beaker immediately due to the formation of PPY. After 10 min, a film with a thickness of $3-4 \mu m$ was formed and removed with a glass or a Teflon plate. Then, a fresh interface appeared and PPY film continued to be produced. A sufficient amount PPY was obtained by repeating the film-removing process described above. As-formed polymer films were rinsed with distilled methanol and dried under a vacuum at 80°C for 12 h. It should be noted here that a very thick film of PPY could not be obtained by this technique. This is most possibly because of the volume limitation of the liquid interfacial layer and the difficulty of the reactants defused through the compact PPY film.

Characterization Techniques

A scanning electron microscopy picture of the film was taken using an X-560 electron micrographer. Infrared spectra were carried out on an IFS-66V FTIR spectrometer (Bruker Co.). The compositions of the films were analyzed by a Perkin–Elmer 240 C elemental analyzer. The thickness of the film was detected by measuring a 10-layered PPY film peeled off from the solid substrate with a "Heilderham" thickness monitor with an accuracy of 2 μ m. The conductivity of the films was measured with a two-electrode technique.

RESULTS AND DISCUSSION

System Selection

The property of the solvents used for interfacial polymerization of PY has a strong influence on the output of the product. First, the two solvents should be mixed with each other a little, leading an interfacial layer in which PY can react with the oxidant; second, the oxidant and the monomer should not be soluble in the same solvent and, thus, the reaction can be restricted at the interfacial area; and third, the density of the upperlayer solvent should be lighter than that of PPY. This makes PPY to remain at the interface, not deposited as a powder at the bottom or floated on the aqueous surface. The property of the oxidant affects not only the polymerization rate of the monomer, but also the morphology of the film. For the water/chloroform system, take FeCl₃ and $(NH_4)_2S_2O_8$ as examples: The polymerization rate of PY with $FeCl_3$ as the oxidant was faster than that of $(NH_4)_2S_2O_8$. This is due mainly to the higher solubility of $FeCl_3$ than of $(NH_4)_2S_2O_8$ in chloroform. However, the film of PPY produced by the oxidation of FeCl₃ was very porous. Only a thick porous PPY cake was formed. On the other hand, the film obtained by using $(NH_4)_2S_2O_8$ as the oxidant was very compact as illustrated by its scanning electron microscopy (SEM) picture shown in Figure 1. On the basis of these considerations, we chose chloroform as the solvent for PY and water as the solvent for oxidant and ammonium persulfate as the oxidant.

Conductivity Measurements

The conductivity of PPY film varied slightly with the molar ratio of PY/(NH₄)₂S₂O₈ ($M_{\rm PY}/M_{\rm O}$, $M_{\rm O}$ = 0.2*M*) as shown in Table I. According to this table, the conductivity of the PPY film increased from 0.11 to 0.14 S/cm as $M_{\rm PY}/M_{\rm O}$ decreased from 10 to 0.5. This is due mainly to the overoxidation of PPY with an increasing oxidant molar ratio. This conclusion was confirmed by elemental analysis and the infrared spectra of the PPY products.

Structure Characterizations

The elemental contents of the films are shown in Table II. It was reported that the contents of sulfur

Table I Conductivity of PPY Films

Conductivity (S/cm)
0.14
0.13
0.12
0.11

$M_{\rm PV}/M_{\rm O}$				
$(M_{\rm O} = 0.2M)$	C (wt %)	H (wt %)	N (wt %)	O + S (wt %)
10	48.68	5.40	13.78	32.14
2	47.25	4.40	12.90	35.45
1	46.38	3.06	12.85	36.71
0.5	45.54	3.60	12.46	38.40

 Table II
 Elemental Contents of PPY Films

in the PPY prepared by oxidation with persulfate salts were very low (about 1-4%, by weight) and could be neglected.⁵ Therefore, the experimental formula of the PPY films listed in Table II can be nearly represented by $C_{4.1-4.3}H_{3.9-5.5}N_{1.0}O_{2.0-2.7}$. The atom number ratios of carbon and nitrogen changed only a little, while those of carbon and oxygen increased dramatically with decreasing $M_{\rm PY}/M_{\rm O}$. These results implied that the decreasing $M_{\rm PY}/M_{\rm O}$ resulted in increasing overoxidation of PPY, and hydrogen atoms in the PY ring had been partly substituted by oxygen. Infrared spectra of the polymer also supported this conclusion. Figure 2 shows the IR spectrum of PPY obtained for $M_{\rm PY}/M_{\rm O}$ = 1. The broad band at $3000-3500 \text{ cm}^{-1}$ could be attributed to N-H and C-H stretching vibrations.^{7,8} These two bands were overlapped and could not be divided clearly. At 1704 cm⁻¹, a strong carbonyl stretching band was found, and the band at 1560 cm⁻¹ could be assigned to a N—H wagging vibration. As $M_{\rm PY}\!/\!M_{\rm O}$ increased from 0.5 to 10, the band-strength ratios of C=O at 1704 cm^{-1} and

those of N—H at about 1560 cm⁻¹ decreased from 1.8 to 0.9 (Fig. 3). These results indicated that the extent of overoxidation of PPY increased by increasing the molar ratio of the oxidant and the monomer. The wavenumber shift of the N—H band (1551–1563 cm⁻¹) resulted from the formation of hydrogen bonds on the PPY backbone.

Thermal Property Tests

The thermal property of the PPY films was measured by differential scanning calorimetry (DSC) tests. According to the curves shown in Figure 4, the PY films did not show apparent glass transitions as do conventional polymers. However, the thermal stability of the films seems depend on the conditions under which they were prepared. For example, sample 1 starts to decompose at a temperature of ~470 K, while sample 4 starts to decompose at a temperature of ~450 K. This was probably due to the high monomer/oxidant ratio that resulted in the low overoxidation of PPY and the increased thermal stability of the film.

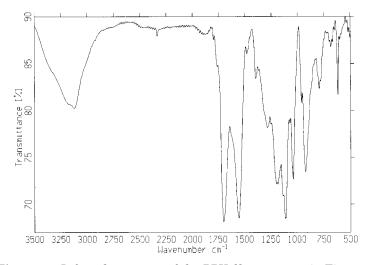


Figure 2 Infrared spectrum of the PPY film, same as in Figure 1.

CONCLUSIONS

PPY films with a thickness of $3-4 \mu m$ can be produced by chemical oxidative polymerization of pyrrole at the interface of chloroform and water with an oxidant of $(NH_4)_2S_2O_8$. Overoxidation of PPY was observed for high concentrations of the oxidant. When the oxidant concentration was controlled, a high monomer concentration in the chloroform phase resulted in PPY with better quality.

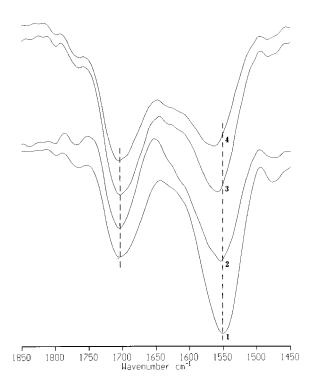


Figure 3 Regional spectra of PPY films prepared from the systems with various $M_{\rm PY}/M_{\rm O}$: (1) 10*M*; (2) 2*M*; (3) 1*M*; (4) 0.5*M*; (5) 0.2*M*.

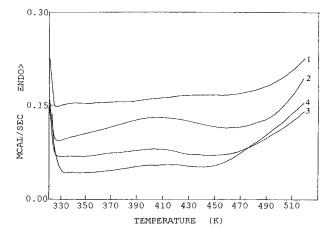


Figure 4 DSC diagrams of PPY films. The numbers of the film are the same as in Figure 3.

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