

# Preparation of Polypyrrole/Polythiophene Double Layers by Electrochemical Polymerization of Pyrrole in the Presence of Thiophene

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## SYNOPSIS

Studies on electrochemical polymerization of pyrrole in the presence of thiophene are given for preparation of polypyrrole (PPy)/polythiophene (PTh) double layers. At a constant current, only pyrrole is electrochemically polymerized in the electrolytic solution containing pyrrole and thiophene in the present experiments. The cyclic voltammograms on pyrrole/thiophene mixtures are similar to that on pyrrole. Preparation of PPy/PTh double layers is carried out by electrochemical polymerization of pyrrole in the presence of thiophene by adding pyrrole and by lowering voltage immediately after electrochemical homopolymerization of thiophene. The resulting double layers show good rectification characters dependent on thickness. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Electrochemical polymerization may facilitate preparation of conductive organic polymers. Among many organic compounds, aromatic heterocyclic compounds such as pyrrole and thiophene are subject to electrochemical polymerization.<sup>1-4</sup> These polymers have a high potential for use in electronic devices. There are some reports<sup>5-7</sup> concerning applications of these polymers to electronic devices. Kaneto et al.<sup>6</sup> succeeded in preparing a polythiophene (PTh)/polypyrrole (PPy) heterojunction, by electrochemical polymerization of thiophene on a PPy film which was polymerized in another electrolytic cell (although we were unable to polymerize electrochemically thiophene on a PPy film<sup>†</sup>). The change of the electrolytic cell in this preparation is attended by air oxidation, which may account for this. To avoid this oxidation, we examined two methods for the preparation of PPy/PTh double

layers without change of the electrolytic cell. In one method (method 1), galvanostatic copolymerization of pyrrole with thiophene was examined, since we expected that pyrrole would be polymerized until consumption of the total amount of pyrrole in the feed and then thiophene would be polymerized, in an electrolytic cell involving pyrrole and thiophene at a constant current. In another method (method 2), electrochemical polymerization of pyrrole in the presence of thiophene was carried out by adding pyrrole and by lowering voltage immediately after the electrochemical homopolymerization of thiophene. In these methods mentioned above, pyrrole needs to polymerize electrochemically in preference to thiophene in the electrolytic solution containing pyrrole and thiophene.

Electrochemical copolymerizations of monomers with mutually similar oxidation–reduction potentials such as pyrrole and substituted pyrrole have been studied.<sup>8,9</sup> However, studies of electrochemical copolymerization of monomers with mutually different oxidation–reduction potentials such as pyrrole and thiophene, to our knowledge, have not been reported. Therefore, we studied also cyclic voltammetry on pyrrole/thiophene mixtures to obtain basic data on electrochemical polymerization of pyrrole in the presence of thiophene.

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† The causes will be described elsewhere.

## EXPERIMENTAL

### Materials

All compounds were purchased from Aldrich. Tetraethylammonium tetrafluoroborate (TEAFB) was recrystallized from ethanol and dried under vacuum. Pyrrole and thiophene were distilled under reduced pressure immediately before use. Acetonitrile was stored over molecular sieves after distillation.

### Cyclic Voltammetry

Cyclic voltammetry was performed in a single-compartment cell connected to another cell including a reference electrode by a salt bridge. A platinum plate, a platinum wire, and saturated calomel were used as the working, the counter, and the reference electrodes, respectively. The solution used for the measurement contained 1.84 mM pyrrole and 3.69 mM thiophene with 0.1M TEAFB (supporting electrolyte) in acetonitrile. The sweep rate was set at 100 mV s<sup>-1</sup>. A Hokuto HA-501 potentiostat/galvanostat, a Hokuto HB-111 function generator, and a Riken X-Y recorder were used for the measurements.

### Preparation of PTh/PPy Double Layers

In method 1, pyrrole and thiophene were galvanostatically copolymerized in a cell system similar to one used for cyclic voltammetry. During operation, the current was kept at 15.0 mA. The potential between the working and the reference electrodes was measured using a Hokuto HA-501 potentiostat/galvanostat. The concentrations of thiophene and pyrrole in the feed were 0.06 and 0.06M (copolymer a) or 0.10 and 0.02M (copolymer b).

In method 2, polymerization of pyrrole in the presence of thiophene followed lowering voltage to 3.2 V and by adding 0.1M pyrrole to the electrolytic solution, immediately after electrochemical polymerization for 10 min at 4.2 V (voltage between the working and the counterelectrodes) in a single compartment cell with 0.1M thiophene and 0.1M TEAFB in acetonitrile. The voltage was supplied by use of a Kenwood PA 18-1.2 DC power supply. The copolymerization time was variously changed. The current was occasionally measured by an IWATSU SC-7404 multimeter.

### Infrared Spectrometry

All IR spectra were obtained for samples in potassium bromide discs by use of a Jasco A-3 IR spectrophotometer. All samples were undoped by im-

mersing them in ammonia aqueous solution for 24 h prior to the measurement.

## RESULTS AND DISCUSSION

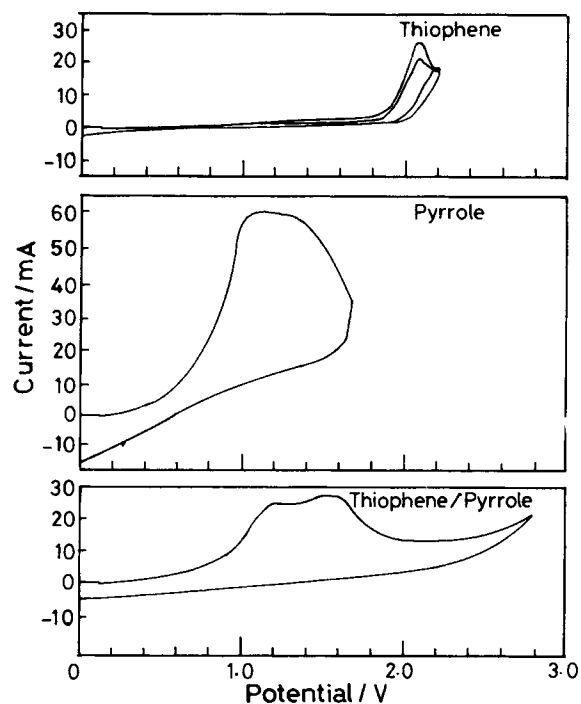
### Cyclic Voltammetry

Figure 1 shows cyclic voltammograms of thiophene, pyrrole, and a thiophene/pyrrole mixture. Those oxidation-reduction reactions seem to be irreversible. The first peak oxidation potentials of thiophene and pyrrole are consistent with those in the literature<sup>1,3</sup> (2.1 V for thiophene, 1.3 V for pyrrole). Only a broad oxidation peak appears in the range of 1.2–1.6 V in the voltammograms of thiophene/pyrrole mixtures, during sweeping potential from 0.0 to 2.8 V. Therefore, the oxidation peak is considered to be due to oxidation only of pyrrole. This suggests that pyrrole is predominantly polymerized in the electrochemical copolymerization of pyrrole with thiophene.

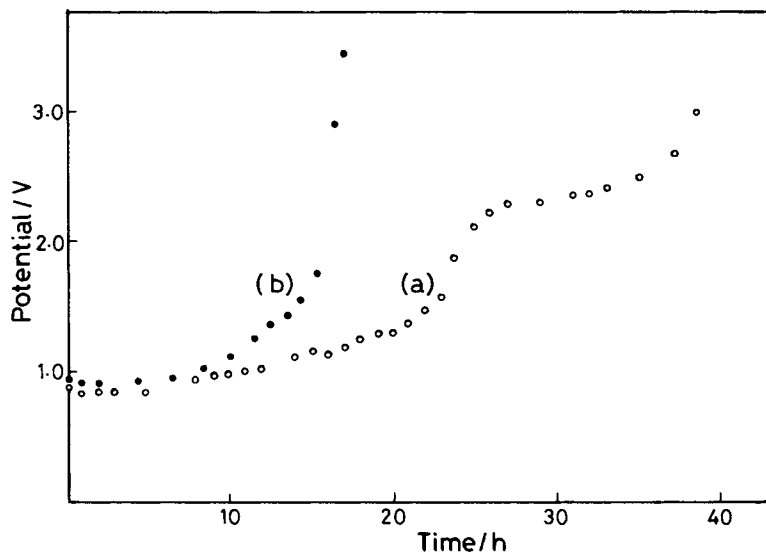
### Electrochemical Copolymerization

#### Method 1

Figure 2 shows the relationship between time and potential in the copolymerization at a constant cur-



**Figure 1** Cyclic voltammograms of thiophene, pyrrole, and a thiophene/pyrrole mixture.



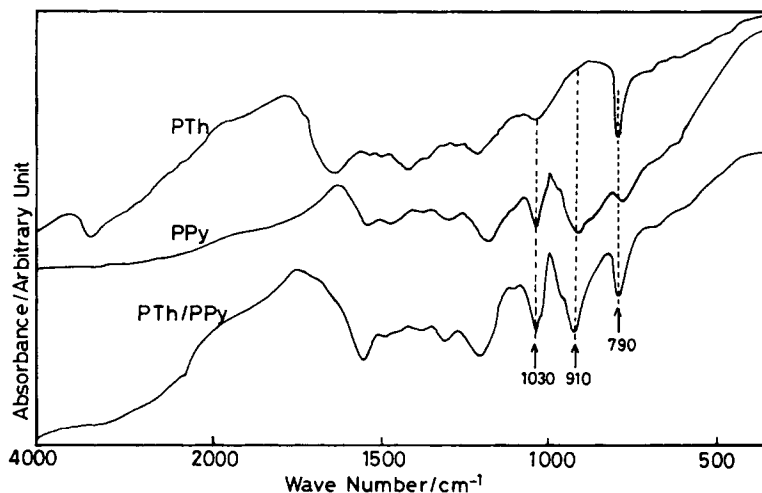
**Figure 2** Relations between time and potential in the electrochemical copolymerization of pyrrole with thiophene at a constant current: (a) 0.06M thiophene, 0.06M pyrrole; (b) 0.10M thiophene, 0.02M pyrrole.

rent. The results of IR spectrometry (all the spectra are similar to the PPy spectrum in Figure 3) and elemental analysis in Table I on the resulting copolymers **a** and **b** suggest that they are almost homopolymers of pyrrole. This is consistent with the results of cyclic voltammetry. It is still an important problem as to whether thiophene reacts at the lower concentrations of pyrrole or not. The faster increase in potential with a lowering concentration of pyrrole suggests a certain occurrence of electrochemical reaction of thiophene. However, it is a fact that the

homolike polymer of pyrrole is yielded by electrochemical copolymerization in an electrolytic solution containing 0.02–0.06M pyrrole and 0.06–0.10M thiophene.

#### Method 2

The current decreased at about a  $0.1 \text{ mA min}^{-1}$  rate from about 8 mA in the polymerizations of pyrrole in the presence of thiophene. Table II shows the thickness of the pyrrole-rich layer for the resulting



**Figure 3** IR spectra of PTh, PPy, and a PTh/PPy double layer.

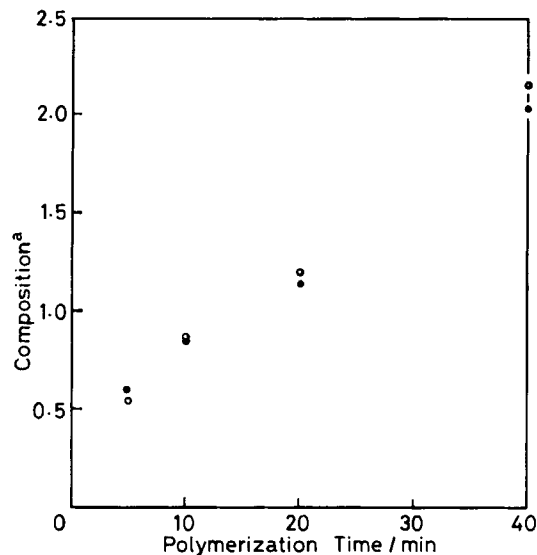
**Table I Elemental Analysis**

Sample	Polymerization Time (h)	Content <sup>a</sup> (mol %)			
		C	H	N	S
Copolymer a	0.5	36.6	37.2	9.1	0.1
Copolymer a	30.0	34.6	38.2	8.9	0.2
Copolymer a	48.0	38.7	36.9	8.6	0.2
Copolymer b	0.5	38.2	37.3	8.6	0.2
Copolymer b	12.0	36.3	37.2	8.2	0.4

<sup>a</sup> About 20 wt % is ash.

PPy/PTh double layers, measured with a micrometer. The growing rate of thickness also decreases with time. We explain these results as follows: Since the voltage between the working and the counter-electrodes is kept constant, the voltage between the surface of PPy layer and the counterelectrode decreases, as the polymerization proceeds. Since the dopant concentration decreases with decreasing voltage,<sup>10</sup> the conductivity and the voltage successively decrease as polymerization proceeds.

IR spectra of the double layers are a mix of the spectra of PTh and PPy, as shown in Figure 3. Ratios of optical densities at 790 and 910  $\text{cm}^{-1}$  were taken in order to determine the PPy/PTh composition by calibration with PPy/PTh mixtures of known composition. Figure 4 shows plots of PPy/PTh composition for the double layers against polymerization



**Figure 4** Relations between PPy/PTh composition of a double layer and the polymerization time of pyrrole (○) in the presence of thiophene or (●) in the absence of thiophene on PTh. 1 mol of pyrrole unit/1 mol of thiophene unit.

time of pyrrole in the presence of thiophene, together with plots of PPy/PTh composition against time of polymerization of pyrrole in the absence of thiophene on the PTh film polymerized electrochemically prior to use. Since all homopolymerizations of thiophene were carried out for 10 min, both the in-

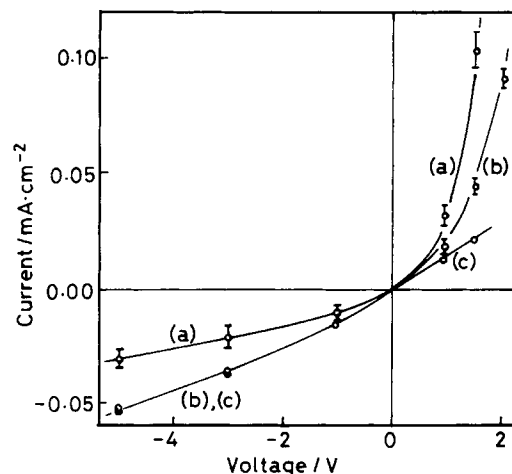
**Table II Preparation of PTh/PPy Double Layers**

Entry	Polymerization Time (min)		Thickness <sup>b</sup> ( $\mu\text{m}$ )	Remarks <sup>c</sup>
	Thiophene	Pyrrole <sup>a</sup>		
1	10	5	16	IR
2	10	10	31	IR
3	10	10	32	IV
4	10	10	34	IV
5	10	10	28	IV
7	10	10	30	IV
8	10	20	50	IR
9	10	20	49	IV
10	10	20	52	IV
11	10	40	76	IR
12	10	40	74	IV

<sup>a</sup> Polymerization time of pyrrole in the presence of thiophene.

<sup>b</sup> Thickness of pyrrole-rich layer measured with a micrometer.

<sup>c</sup> Used for measurement of IR spectrum or IV characteristic.



**Figure 5** IV characteristics of PPy/PTh double layers: (a) polymerization time of pyrrole, 10 min; (b) polymerization time of pyrrole, 20 min; (c) polymerization time of pyrrole, 40 min. The plots depict the mean value and the standard deviation for samples.

crements of PPy content at the same polymerization time seem to agree. This suggests that PPy-rich layers of PPy/PTh double layers consist only of PPy. The thickness is also determined from the PPy/PTh composition. The values of thickness, obtained from micrometer measurements, are larger than those obtained from IR spectra, perhaps because of unevenness of the surface.

### Conductivity

Figure 5 shows the IV characteristics for PTh/PPy double layers with various thicknesses of the PPy-rich layer. The double layers with about 30  $\mu\text{m}$  thickness show good rectification characteristics. However, with increasing thickness of the PPy layer, the IV characteristics become ohmic. This is explained in terms of a decrease in conductivity as of polymerization of the PPy layer proceeds, i.e., with increasing thickness of the PPy layer: The decrease in conductivity of the PPy layer causes disappearance of the voltage drop of PPy/PTh junctions.

### REFERENCES

1. A. F. Diaz, K. K. Kanazawa, and G. P. Gardin, *J. Chem. Soc. Chem. Commun.*, 635 (1979).
2. K. Kaneto, Y. Kohno, K. Yoshino, and Y. Inuishi, *J. Chem. Soc. Chem. Commun.*, 382 (1983).
3. R. J. Waltman, J. Bargon, and A. F. Diaz, *J. Phys. Chem.*, **87**, 1459 (1983).
4. R. J. Waltman, A. F. Diaz, and J. Bargon, *J. Electrochem. Soc.*, **131**, 1452 (1984).
5. J. H. Kaufman, T. C. Chung, A. J. Heeger, and F. Wudl, *J. Electrochem. Soc.*, **131**, 2092 (1984).
6. K. Kaneto, S. Takeda, and K. Yoshino, *Jpn. J. Appl. Phys.*, **24**, L553 (1985).
7. A. Tsumura, H. Koezuka, and T. Ando, *Syn. Met.*, **25**, 11 (1988).
8. H. Koezuka and S. Etoh, *J. Appl. Phys.*, **54**, 2511 (1983).
9. N. Kumar, B. D. Malhotra, and S. Chandra, *J. Polym. Sci. Polym. Lett. Ed.*, **23**, 57 (1985).
10. K. Kaneto, S. Hayashi, S. Ura, and K. Yoshino, *J. Phys. Soc. Jpn.*, **54**, 1146 (1985).

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