Modification of Polyindole by the Incorporation of Pyrrole Unit

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ABSTRACT: Electrochemical copolymerization of pyrrole and indole was performed galvanostatically in a solvent of acetonitrile (AN)/water (vol %: 99/1). The product obtained was characterized by cyclic voltammetry and infrared spectroscopy. The influence of the monomer feed ratio of pyrrole and indole on the synthesis of the copolymer was investigated. The amount of pyrrole units in the copolymer chain increased with increase of the concentration of the pyrrole monomer in the solution. The results showed that the electrochemical activity of the copolymer was improved as the incorporation of pyrrole units increased. Thermogravimetric analysis was carried out to investigate the properties of the copolymer. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 814–820, 2002

Key words: conducting polymers; copolymerization; electrochemistry; FTIR; TGA

INTRODUCTION

Electronically conducting polymers have received much attention in recent years. These materials have a large number of applications, such as in light-emitting diodes,[1] electrochemical supercapacitors,[1] sensors,[2] batteries,[3] electrochromic displays,[4] memory-storage devices,[5] ion gates,[6] nonlinear circuit elements,[7] and dispensers of pharmacologically active reagents.[8] The main motivation for studying copolymers is to obtain materials that display better properties and to overcome the limitations of the rareness of new conjugated-bond-containing monomers.

Among the conducting polymers that have conjugated double bonds, polyindole (Pin) has received little attention because it has some short-comings: It is hard to obtain free-standing Pin film and the electroactive capacity of Pin is much lower than that of other conducting polymers such as polypyrrole (Ppy) and polythiophene (Pth).

In this article, we report on the modification of Pin by the cooperation of the pyrrole (Py) unit during the electropolymerization process. The copolymer composition can be controlled by the feed ratio of the monomers and characterized by Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA). The copolymer showed much higher electrochemical activity than that of pure Pin.
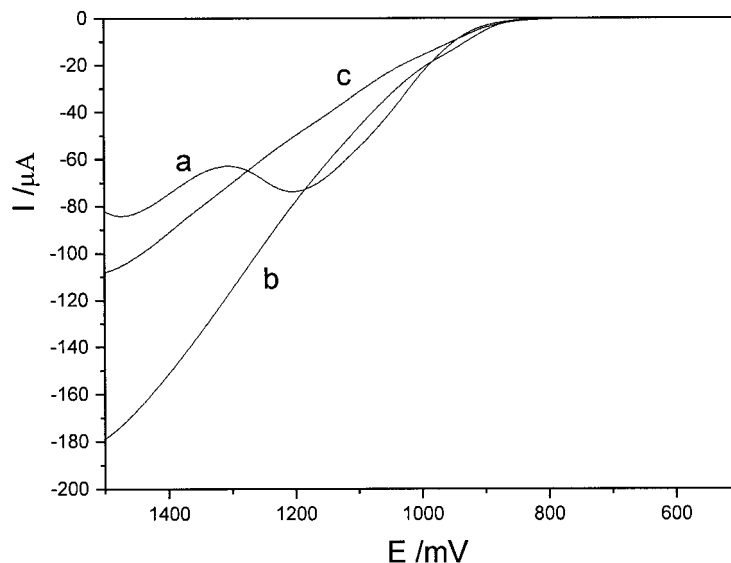
EXPERIMENTAL

Chemicals

Py (Aldrich, 99%) was distilled under a nitrogen atmosphere just before use. Indole (In) was dried in a vacuum oven at 25°C for 24 h. Acetonitrile (AN) was purified according to the literature.[9]

Figure 1 Current–potential curves of (a) 0.08M In, (b) 0.1M Py, and (c) 0.08M In + 0.1M Py in AN/water (vol % 99/1) + 0.1M LiClO$_4$. Scanning rate: 100 mV s^{-1}. Reference electrode: Ag/AgCl/0.1M KCl.

Lithium perchlorate (LiClO$_4$) was dried in a vacuum oven at 80°C for 24 h.

Electrochemistry Preparations and Characterizations

All the samples were grown in an AN/water (vol %: 99/1) solution containing 0.1M LiClO$_4$ as a supporting electrolyte. The electropolymerization was performed galvanostatically, which is discussed in a later section. The electrochemical cell used was a one-compartment, three-electrode system used with a PARC M273 potentiostat under the control of a computer at room temperature. A stainless-steel plate (4.0 × 2.0 cm^2) was used as the counterelectrode and the reference electrode was a Ag/AgCl/0.1M KCl electrode. A stainless plate (4.0 × 2.0 cm^2) was used as the working electrode to deposit the precipitates and a platinum disc (1.96 × 10^{-3} cm^2) was used as the working electrode to investigate the electrochemical behavior of the copolymer. The working electrode was polished by diamond paste (1.5 μm) and then cleaned in an ultrasonic acetone bath before use. The solution was deaerated by argon bubbling carefully before each electrochemical experiment and maintained under a slight argon overpressure during the experiment. The sample that had been moved from the electrode was rinsed with acetone and dried in a vacuum oven for 2 days until a constant weight was achieved. The

platinum disc with precipitates was dried in air and then put into a blank solution composed of 0.1M LiClO$_4$ and AN to obtain the cyclic voltammograms.

Spectroscopy Experiments

FTIR spectra was recorded by an IFS-660 spectrometer (Brucker, Germany).

Thermal Analysis

TGA was performed in an SDF2960 thermal analyzer (TA Instruments, U.S.A.). TGA measurements were done under a nitrogen atmosphere at a temperature from 25 to 800°C at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Electrochemistry

Current–potential curves taken in a quiet solution at a potential sweep rate of 100 mV s^{-1} are given in Figure 1. It should be noticed that the background electrolyte is electrochemically silent in the whole potential range. It can be seen that the polymerization threshold (i.e., the lowest potential needed to allow the growth of a polymer layer) of In is 0.90 V versus Ag/AgCl/0.1 M KCl
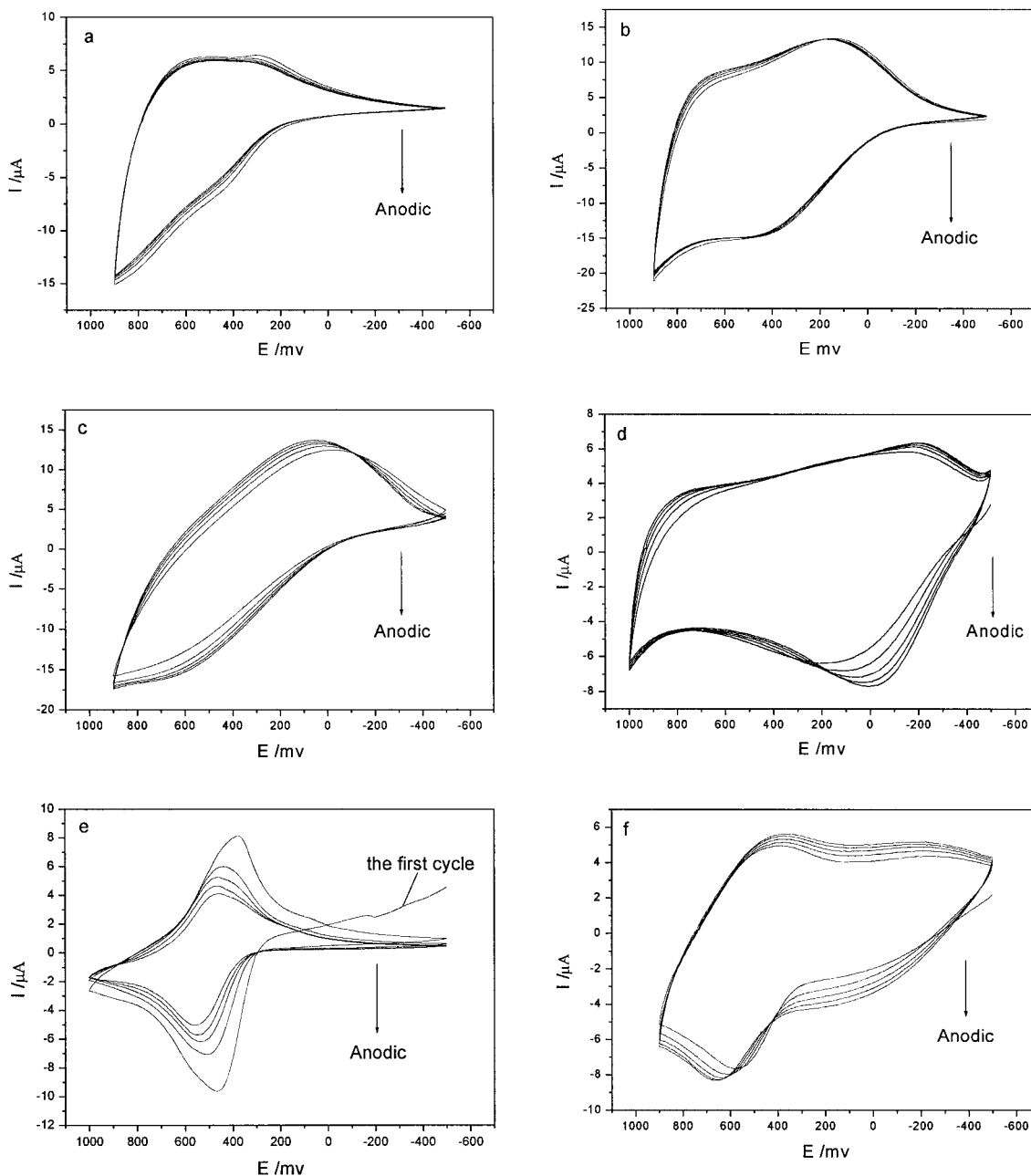
Figure 2 CVs recorded in AN/water (vol %: 99/1) + 0.1M LiClO$_4$ solution of In:Py = (a) 8:5, (b) 4:5, and (c) 2:5 (mol, In = 0.08M), (d) pure Py (0.1M), (e) pure In (0.08M), and (f) bilayer (Ppy–Pin) (0.1M Py–0.08M In). Scanning rate: 100 mV s^{-1}. Reference electrode: Ag/AgCl/0.1M KCl. Polymerization current: 1 mA/cm^2.

and that of Py is 0.83 V versus Ag/AgCl/0.1 M KCl. The small distinction (0.07 V) between the oxidation potential of the two monomers suggests a great possibility of the copolymerization of the two monomers. When a current potential curve was taken in a AN/water (V %: 99/1) containing 0.08M In and 0.1M Py, curve (c) was obtained.

The current of curve (c) is smaller than that of (b) (Py) but a little larger than that of curve (a) (In). This may due partly to a side reaction, which will lower the oxidation current. In this situation, the side reaction of Py is small, but that of In is much greater. So, when Py and In coexist in a solution, the polymerization efficiency will decrease, com-

Table I   Redox Peak Values of the Polymer Prepared in a Solution of AN/Water (Vol %: 99/1) + 0.1M LiClO$_4$ Containing Different Amounts of Pyrrole + 0.08M Indole

Feed Ratio (In:Py)	Indole (0.08M)	8 : 5	4 : 5	2 : 5	Pyrrole (0.1M)
Polymerization time	60 min	60 min	60 min	60 min	10 min
Anodic potential (mV)	560	440	394	563	−22
Cathodic potential (mV)	467	306	125	−71	−233
Anodic current (μA)	−5.2	−5.3	−14.0	−14.6	−7.6
Cathodic current (μA)	4.0	6.0	13.3	13.6	6.2
Anodic charge (μC)	−37.29	−101.3	−216.3	−135.1	−123.3
Cathodic charge (μC)	67.61	89.69	192.8	142.6	116.9

Polymerization current: 1 mA/cm^2.

pared with that of pure Py, although it is larger than that of pure In.

Electrochemical copolymerization with different feed ratios of the monomers was studied. Figure 2(a–d) shows the cyclic voltammograms (CVs) of the different concentrations of the Py monomer which ranged from 0.05 to 0.2M, respectively. An interesting character of the CVs is that the redox potential of the copolymers shifts to higher potentials with an increasing of the feed ratio (In:Py, mol). When the ratio is 8:5, the copolymer shows an anodic peak at 440 mV and a cathodic peak at 306 mV, which is the closest to pure Pin; when the ratio (In:Py) is 2:5, the copolymer shows a cathodic peak at −70 mV, which is the closest to pure Ppy. This indicates that more Py units are incorporated into the copolymer with an increased feed ratio. So, the copolymer exhibits properties like those of Ppy, which results in a potential shift. The current peak values of the copolymer prepared in different concentrations of Py are listed in Table I, together with the values of the peak potentials. In addition, it must be noticed that the CV of the bilayer (Ppy–Pin composites), which is made by successive polymerization of Ppy and Pin, is merely the sum of the voltammograms of Pin and Ppy, as shown in Figure 2(f). It is quite different from those of the copolymers, definitely suggesting that the copolymerization is performed on the electrode.

Furthermore, another noticeable feature is that, compared with pure Pin, the electrochemical activity of the copolymers is much higher after the same time of polymerization. When the Py units are incorporated, not only does the peak current increase, but also the CVs remain stable, which represents little change of the electrochemical activity, when the polymerization time is 1 h in each process, as shown in Figure 2. The activity

of Pin [Fig. 2(e)] decreases rapidly: The cathodic current decreases from 9 to 5 μA in the first five-cycle scanning, while the anodic current decreases from 7 to 4 μA; when the feed ratio is 4:5 [Fig. 2(b)]. The cathodic current (14 μA) and the anodic one (13 μA) both increase more than twice and remain steady during the scanning process, as does Ppy. Obviously, the peak current increases as the concentration of Py increases. These results illustrate that the incorporation of Py units has improved the electrochemical activity of Pin.

The voltammetric charge data are also given in Table I, which provides more evidence confirming the improvement of the electrochemical activity. The electrochemical activity of Pin is much lower than that of Ppy, which infers that the electrochemical active sites in Pin are much less than those of Ppy if the same length is assumed. So, adding the Py units into the copolymer will increase the number of electrochemical active sites in the polymer and, hence, increases the electrochemical activity. However, for the copolymer (2:5), the charge slightly decreases. This may be caused by the patent change from powder (4:5) to film (2:5), which leads to the decreasing of the electrochemical activity.

Spectroscopy Experiments

The FTIR spectra of the copolymers deposited galvanostatically with the concentration of Py varied from 0.05 to 0.2M are compared with those of pure Ppy, pure Pin, and a bilayer in Figure 3. An impressive characteristic is the evolution of the absorption bands located around 3334 cm^{-1}, as shown in Figure 3(A). In the spectrum of Pin, the single peak is assigned to the stretching of N—H.[10] In the spectra of the copolymers, this
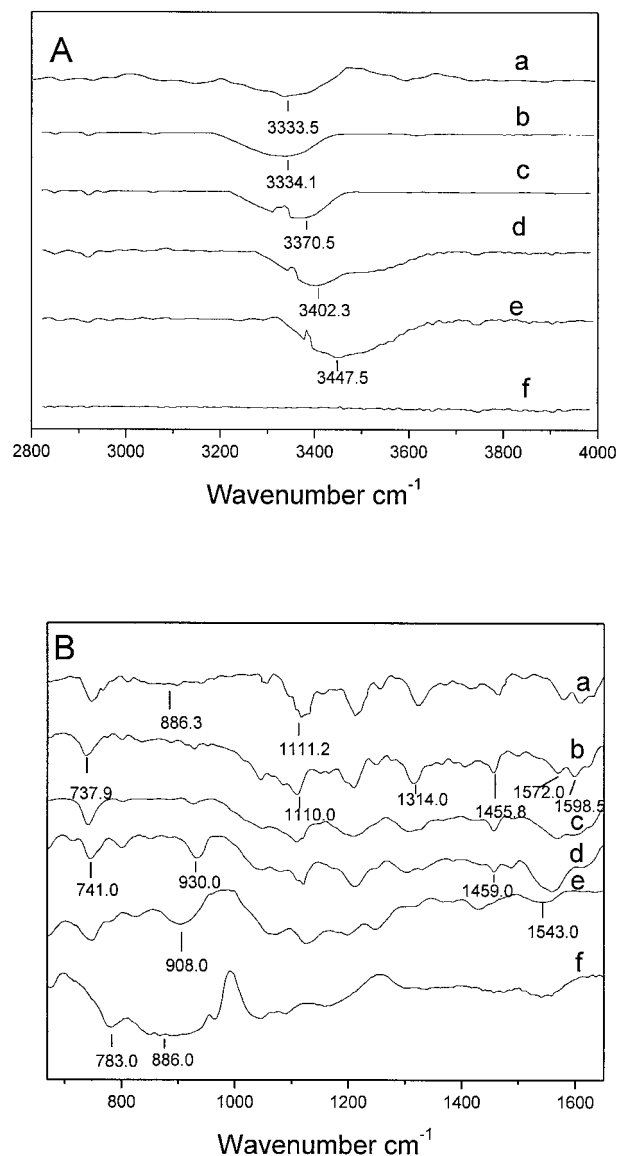
Figure 3 (A,B) Infrared spectra of (a) bilayer (Pin–Ppy), (b) pure Pin, (c) 8:5, (d) 4:5, (e) 2:5, and (f) pure Ppy from the solution of AN/water (vol %: 99/1) + 0.1M LiClO$_4$ galvanstatically.

peak is similar to that of Pin in shape and shifts to high frequency with increasing Py, while in the spectra of Ppy this peak disappears, indicating coupling when polymerization does not involve all the N atoms in the In units. This result is in agreement with previous suggestions.[11] Moreover, another noticeable feature in the spectra is that an absorption band appeared around 784 cm^{-1} both in pure Ppy and the copolymers, which is a characteristic of α-substituted five-membered hetercyclic compounds, suggesting that the α-position of each polymer is involved in the copoly-

merization.[12] These characteristics were indicated in the spectrum of the bilayer.

The evolution of the bands in the fingerprint region with increase of the concentration of Py is also interesting. In the spectrum of Pin, the single peak located at 1456 cm^{-1} is assigned to the stretching of the benzene ring, which moves to a low frequency in this condition; the peak at 1110 cm^{-1} is attributed to the vibration of C—N; the peak at 738 cm^{-1} is induced by out-of-plane C—H deformation; and the peak at 1314 cm^{-1} is induced by the stretching (C—N) of anime.[13] All these peaks appear in the spectra of the copolymer, but their intensity decreases with increasing of the concentration of Py, which infers the decrease of the In units incorporated into the copolymer. Another interesting feature that must be noticed is the evolution of bands around 900 cm^{-1} in the spectra of the copolymer, which is due to the C—H deformation of 2,5-substituted Py.[14] In the copolymers, the intensity of these bands increase with increasing of the Py monomer in the solution, but the center of the peak moves from 886 cm^{-1} (Ppy) to 908 cm^{-1} (feed ratio 2:5), a difference of 22 cm^{-1}, and to 930 cm^{-1} (feed ratio 4:5). They also differ, apparently, from those absorption peaks of the bilayer in this region, whose composites are Ppy and Pin. It may be regarded as evidence of copolymerization, distinguishing itself from the simple addition of the spectra of Pin and Ppy. This result indicates that the amount of Py units incorporated into the copolymer increases with an increasing feed ratio (In:Py), which is in accordance with the conclusion of the CVs.

Thermal Analysis

The thermal properties show some distinctness: Figure 4(A) shows the TGA curves of the copolymer with the pure polymers: Pin and Ppy. It is clear that Pin begins to lose its weight about 220°C (losing 92%), while Ppy undergoes degradation at a temperature of 300°C (losing 92%), implying that Ppy is more stable than is Pin when being heated. But the copolymer (4:5) starts to decompose at the temperature of 150°C, lower than that of both pure polymers. This can also be seen clearly from the change of the maximum reaction rate (R_{max}), as shown Figure 4(B). The maximum reaction rate of the Py units in the copolymer occurs at almost the same position, while that of In units occurs much earlier than that of the pure polymer. This may due to the shorter chains, on average, of In units in the
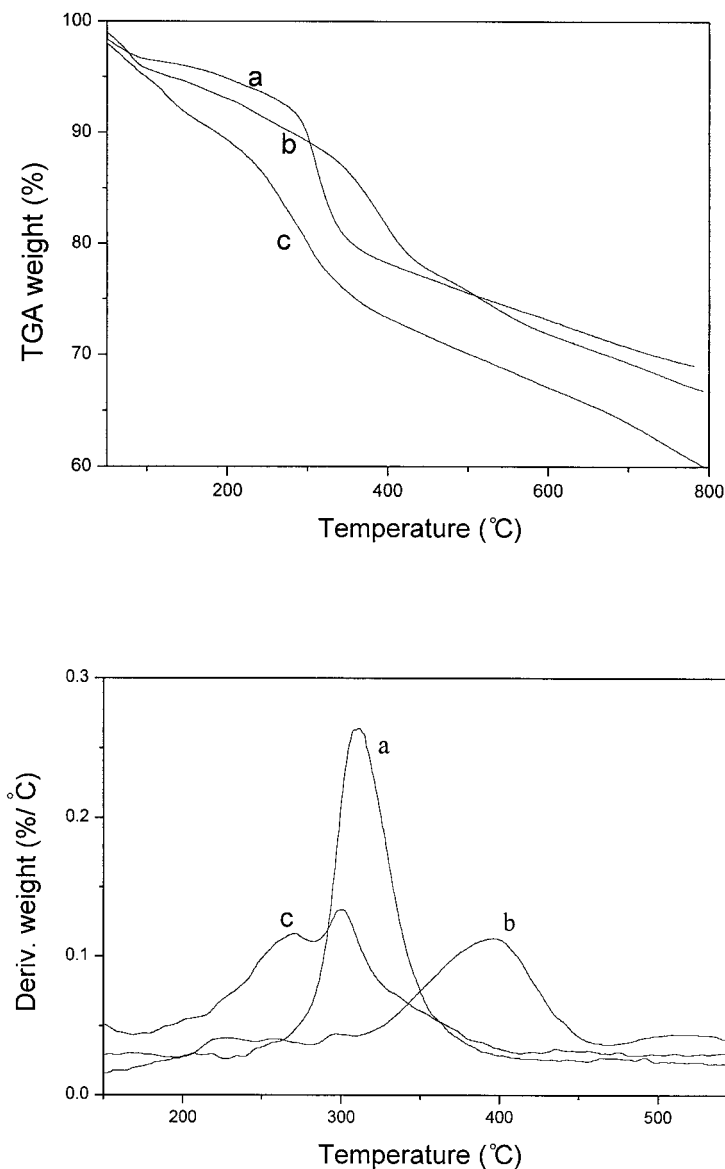
Figure 4 (A) TGA curves; (B) temperature dependencies of the reaction rates of (a) pure Ppy, (b) pure Pin, and (c) feed ratio 4:5 obtained from the solution of AN/water + 0.1M LiClO$_4$.

copolymer, which can be explained by the difference of the activity of the radical cations as its electrooxidation mechanism.

CONCLUSIONS

Electrochemical copolymerization of Py and In was successfully realized in an AN/water (vol %: 99/1) solution containing 0.1M LiClO$_4$ as the supporting electrolyte by the galvanostatical method, which indicates that this electrode reaction is reversible and the copolymer has intermediate properties between pure Ppy and pure Pin. The factor that affects the composition of the copolymer was tested and the results show that the higher is the monomer–feed ratio (In:Py), the more In units are incorporated into the copolymer, while the oxidation potential of the two monomers is close to each other.

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