

Electrochemical Copolymerization of Pyrrole and Propylene Oxide

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ABSTRACT: A copolymer of pyrrole and propylene oxide was synthesized by an electrochemical method. The product was confirmed to be a copolymer by electrochemical and spectral experiments. The influences of the electrode materials and solvents on the copolymerization were explored. A

probable mechanism was proposed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2624–2627, 2003

Key words: conducting polymers; electrochemistry; copolymerization; polypyrroles

INTRODUCTION

The electrochemical synthesis of conducting polymers¹ has become an important field of polymer science. With this method, many kinds of conducting polymers, including polyaniline,² polypyrrole (PPy),³ and polythiophene,⁴ can be synthesized on the surfaces of electrodes directly at room temperature.¹ Among these polymers, PPy has received a great deal of attention because of its high electrical conductivity and environmental stability.¹ However, many potential applications of PPy as conducting polymers have been limited because of its poor mechanical properties and processability. Blending with an insulating polymer is one approach to improving the physical properties of PPy.^{5,6} However, most of these composites and blends gradually lose their conductivity with aging.⁷ The copolymerization of pyrrole (Py) and general monomers is another method of improving the physical properties of PPy. Moreover, the copolymer physical and chemical properties are more stable than the blend properties on account of the covalent bond linkage between different matrices. Some copolymers of Py and styrene, Py and tetrahydrofuran, and so forth have been synthesized and studied.^{7–9} However, all these synthesis methods are complicated, and the reaction conditions are strict, except for Jin's method.⁷ This may limit the applications of these new kinds of copolymers.

In this work, we synthesized flexible copolymer films of Py and propylene oxide (PO) directly onto the surfaces of electrodes and studied the influences of the

electrode materials and solvents on the polymerization. The copolymer of Py and PO was characterized with Fourier transform infrared (FTIR), elemental analysis, and so forth.

EXPERIMENTAL

Chemicals

Py (Fluka) was distilled under reduced pressure before use. Nitromethane, 1,2-dichloroethane, acrylonitrile (AN), and PO were refluxed with CaH₂ for 8 h and then were distilled and stored with CaH₂. Bu₄NBF₄ was a commercial reagent and was used without purification.

Electrochemical experiments

All the electrochemical experiments were carried out in a one-compartment, three-electrode cell with a PE PARC 283 potentiostat/galvanostat under the control of a computer at room temperature. For the determination of the effects of electrode materials on the polymerization, an indium tin oxide (ITO) conducting glass plate and a Pt plate were used as working electrodes. The Pt plate was used as a counter electrode. All the potential values were referred to Ag/AgCl (saturated KCl). Nitromethane, 1,2-dichloroethane, and AN were used as solvents, and Bu₄NBF₄ was used as the supporting electrolyte. Each solution was degassed with bubbling argon before the experiment, and a slight argon overpressure was maintained during the experiments.

Characterization of the polymer

The obtained polymer was washed with acetone for the removal of the solvent and was extracted with

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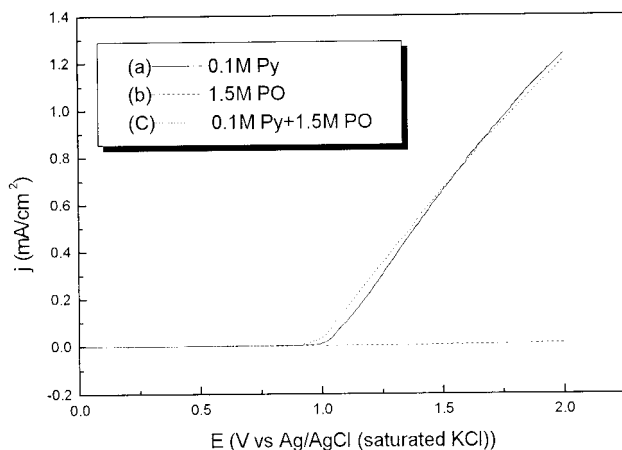


Figure 1 Anodic polarization curves of (a) 0.1M Py, (b) 1.5M PO, and (c) 0.1M Py and 1.5M PO, all in nitromethane containing 0.05M Bu_4NBF_4 at a scan rate of 50 mV/s.

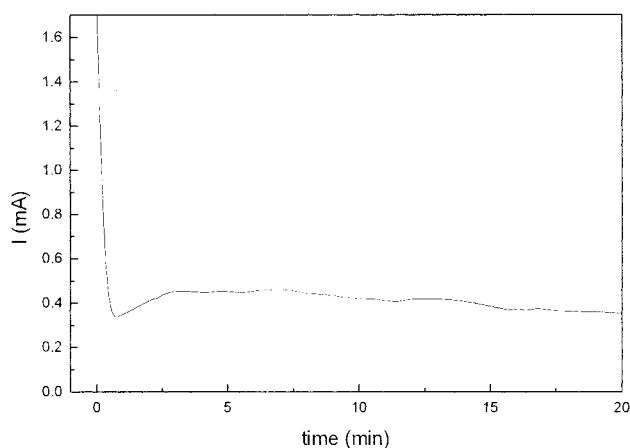


Figure 2 Current-time curve of 0.1M Py and 1.5M PO in nitromethane containing 0.05M Bu_4NBF_4 at a constant potential of 1.5 V.

CH_2Cl_2 for 24 h; it was then dried *in vacuo* at 40°C. The conductivity of the polymer was measured by a four-probe method. The FTIR spectra of the polymer were obtained on a Bruker IR spectrometer after the polymer was ground with KBr and pressed into pellets.

RESULTS AND DISCUSSION

Figure 1 shows the anodic polarization curves of 0.1M Py, 1.5M PO, and 0.1M Py and 1.5M PO in nitromethane. With the potential rising, the curve for 0.1M Py has a threshold at 1.0 V. According to ref. 1, this indicates that Py is oxidized into radical cations and polymerizes above 1.0 V. However, the curve for 1.5M PO does not change under the same conditions. This shows that PO cannot be oxidized. Moreover, after a 1.5M PO nitromethane solution is electrolyzed at a constant potential of 1.5 V for about 2 h, no product polymer is obtained. All these results confirm that PO cannot homopolymerize under these reaction conditions. The curve for 0.1M Py and 1.5M PO has a threshold value similar to that of the curve for 0.1M Py. This indicates that polymerization can happen in a mixture solution of Py and PO.

A nitromethane solution of 0.1M Py and 1.5M PO is electrolyzed at a constant potential of 1.5 V for about 20 min. The current-time curve is shown in Figure 2. With the time elapsing, the current becomes smaller gradually. This phenomenon is different from the electrochemical polymerization of Py.¹ It indicates that the product on the electrode has a lower conductivity than PPy. The polymer film deposited on the working electrode (ITO) is gray, half-transparent, and flexible. The thickness of the film is about 4–9 μm . The product is treated with acetone and then extracted by CH_2Cl_2 for 24 h. The FTIR spectra of the Py-PO copolymer, PPy, and poly(propylene oxide) (PPO) are shown in Figure 3. The spectrum of PPO shows C—H stretching bands

at 2849 and 2922 cm^{-1} and C—O—C stretching bands around 1100 cm^{-1} , whereas the spectrum of PPy shows no significant bands at 2800–3000 cm^{-1} . However, it shows strong bands at 1084 and 1041 cm^{-1} , which are assigned to an in-plane deformation vibration of the Py ring, and a skeletal vibration of the Py ring at 1544 cm^{-1} . In the spectrum for the Py-PO copolymer, strong bands appear at both 2800–3000 and 1544 cm^{-1} . This indicates that the polymer contains segments of both PPO and PPy. The results of an elemental analysis (Table I) confirm that a copolymer of Py and PO has been prepared. It shows that the molar ratio of Py units to PO units is about 0.6:1.

The copolymer film composition varies with the ratio of Py to PO in the polymerization solution. Table I also shows the conductivity of the copolymer, which is in the range of 2.5×10^{-2} to 2.4×10^{-3} S/cm when the composition (Py/PO) of the copolymer changes

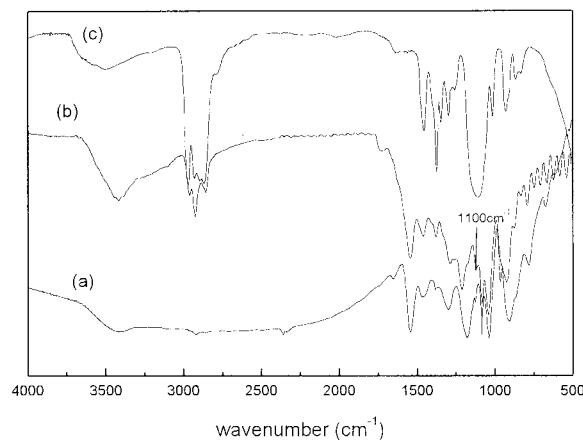


Figure 3 FTIR spectra of (a) PPy at a constant potential of 1.5 V (0.1M Py in CH_3NO_2 containing 0.05M Bu_4NBF_4), (b) Py-PO copolymer at a constant potential of 1.5 V (0.1M Py and 1.5M PO in CH_3NO_2 containing 0.05M Bu_4NBF_4), and (c) PPO synthesized by a rare-earth catalyst.¹⁰

TABLE 1
Composition (Py/PO) and Conductivity of the Py-PO Copolymer Prepared Potentiostatically at 1.5 V
in Nitromethane Containing 0.05 M Bu₄NBF₄

Concentration of the monomer (mol/L)		Elemental analysis of the copolymer			Py/PO ^a (molar ratio)	Conductivity of the copolymer (S/cm)
Py	PO	%C	%H	%N		
0.1	0.1	53.51	5.22	10.28	1.44	2.5×10^{-2}
0.1	0.3	51.75	5.82	7.59	0.75	5.2×10^{-3}
0.1	0.6	56.30	3.42	7.71	0.66	4.7×10^{-3}
0.1	1.0	53.22	5.59	7.23	0.65	4.6×10^{-3}
0.1	1.5	56.54	3.63	7.50	0.62	2.9×10^{-3}

^a The composition of the copolymer (Py/PO) was calculated from the results of elemental analysis.

from 1.44 to 0.62. This indicates that the copolymer is a classic semiconductor.

In the experiments, we discovered that electrode materials affected the copolymerization obviously. Under the same conditions, a film deposited on a Pt electrode is black and nontransparent. However, a film on ITO is gray and half-transparent. In a comparison of their FTIR spectra (Fig. 4), bands at 2800–3000 cm⁻¹ are not found in the spectrum of the product on the Pt electrode. This shows that the content of the PPO segment in the copolymer is too small to be detected.

The effect of the solvent on the copolymerization has been examined as well. Nitromethane, 1,2-dichloroethane, and AN have been used as polymerization solvents. The FTIR spectra of the films synthesized in the three solvents are shown in Figure 5. According to the spectra [Fig. 5(b,c)], the polymers synthesized in nitromethane and 1,2-dichloroethane are similar and have obvious bands of PPO (2800 cm⁻¹ to 3000 cm⁻¹) and PPy (1540 cm⁻¹). However, the polymer synthesized in AN is more likely to be the homopolymer of Py or the copolymer containing a very small amount

of PPO [Fig. 5(a)]. This indicates that the solvents, which have polarity and weak nucleophilicity (nitromethane and 1,2-dichloroethane), are beneficial to the polymerization of PO. Because the copolymer contains a flexible segment of polyether, the physical properties of the copolymer may be better than those of PPy. In addition, the bond of C—O—C has good affinity to some biochemical reagents such as enzymes, so the copolymer may be used as a material for an immobilizing enzyme to make a biosensor.

A probable mechanism is proposed in Scheme 1. It is well known¹ that Py can electrochemically be oxidized into a radical cation that then homopolymerizes and forms a polymer on the surface of the electrode. Moreover, PO cannot electrochemically be polymerized under that condition. It is possible that the radical cation of Py or its oligomer may initiate the polymerization of PO because PO can be initiated by a cationic catalyst¹¹ and nitromethane and 1,2-dichloroethane can induce the polymerization of PO with Py.

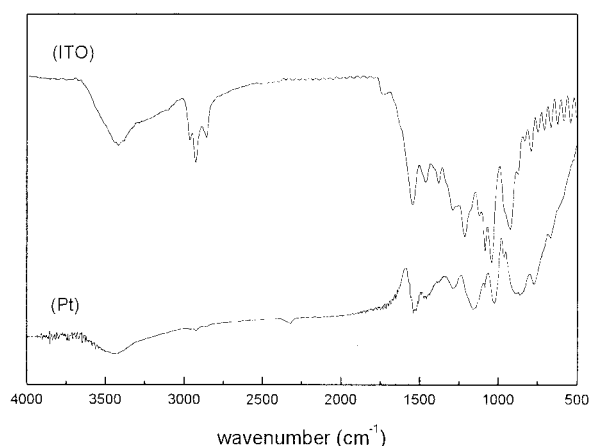


Figure 4 FTIR spectra of the Py-PO copolymer. The polymerization was carried out at 1.5 V in CH₃NO₂ containing 0.1M Py, 1.5M PO, and 0.05M Bu₄NBF₄ on different electrodes.

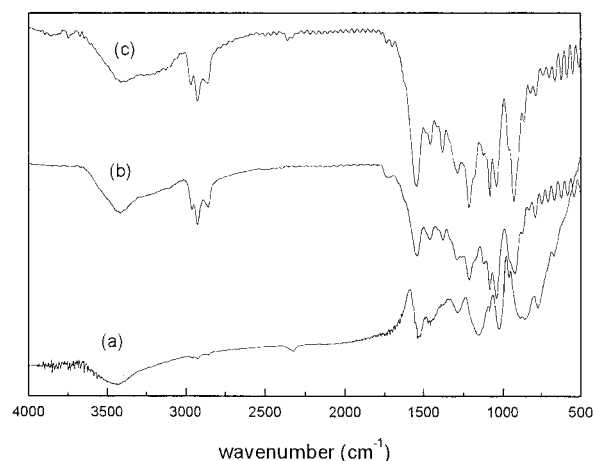
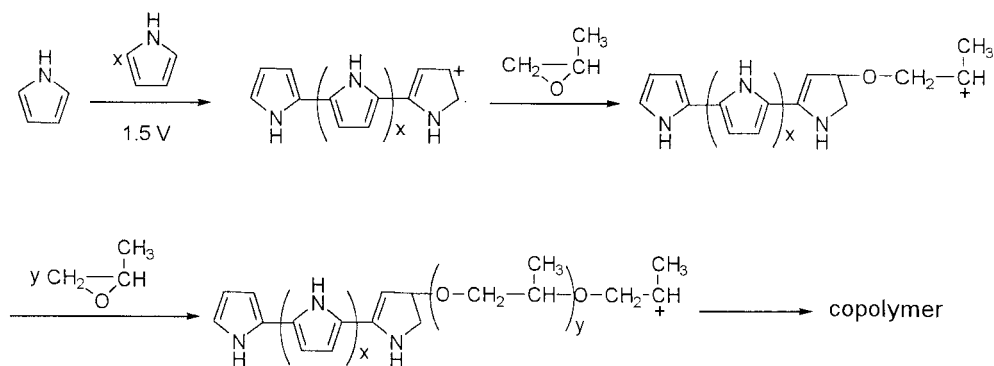


Figure 5 FTIR spectra of the Py-PO copolymer at a constant potential of 1.5 V with 0.1M Py and 1.5M PO containing 0.05M Bu₄NBF₄ in different solvents: (a) AN, (b) nitromethane, and (c) 1,2-dichloroethane.



Scheme 1 Possible mechanism of Py and PO copolymerization.

CONCLUSIONS

A Py/PO copolymer has been obtained successfully through a convenient electrochemical polymerization. The copolymerization is probably initiated by a radical cation. The conductivity of the copolymer is about 10^{-2} to 10^{-3} S/cm, varying with the molar ratio of Py units to PO units. Further work on these films is in progress, and the results will be published in the near future.

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