Polymer Vol. 37 No. 7, pp. 1289–1291, 1996

0032-3861/96/$15.00+0.00

Chemically oxidative synthesis and hydrolysis of poly[1-(2-cyanoethyl)pyrrole]

Takeshi Yamauchi*, Katsunori Kojima, Katsuhisa Tanaka, Tomomi Unuma, Masato Shimomura and Shinnosuke Miyauchi
Department of Bioengineering, Nagaoka University of Technology, Kamitomioka, Nagaoka 940-21, Japan
(Received 15 June 1995; revised 10 July 1995)

1-(2-Cyanoethyl)pyrrole was chemically polymerized in acetonitrile by using iron(III) perchlorate as an oxidizing agent. Poly[1-(2-cyanoethyl)pyrrole] obtained as black powder was hydrolysed with potassium hydroxide to convert cyano groups of the polymer to carboxyl groups. The hydrolysis of the cyano groups was confirmed by means of i.r. spectroscopy. The electric conductivities of these polymers were investigated and it was shown that poly[1-(2-cyanoethyl)pyrrole] behaved as a conductive polymer while the hydrolysed polymer behaved as an insulator.

(Keywords: poly[1-(2-cyanoethyl)pyrrole]; hydrolysis; chemically oxidative polymerization)

Introduction

Polypyrrole is well known as an electrically conducting polymer and is synthesized by both chemical[1–5] and electrochemical methods[6,7]. Modification of polypyrrole with biological materials such as enzymes, antibodies and antigens is an attractive approach in their application as biosensors[8–10].

1-(2-Cyanoethyl)pyrrole possesses a reactive cyano group which can be easily hydrolysed to a carboxyl group and, therefore, can give a new functional conducting polymer. For instance, pyrrole covalently modified with enzymes was prepared by the amido bonding between amino groups of the enzymes and the carboxyl groups obtained by hydrolysis of the cyano groups of 1-(2-cyanoethyl)pyrrole, which was electrochemically polymerized to give the polypyrrole carrying the enzyme[11,12]. However, there are few research works about chemically oxidative polymerization of 1-(2-cyanoethyl)pyrrole and its electrical properties. In this paper, the chemically oxidative polymerization of 1-(2-cyanoethyl)pyrrole and the hydrolysis of the cyano groups of poly[1-2(cyanoethyl)pyrrole] (PPy-Et-CN) are studied. The electrical properties of polymers are also studied for application to electronic devices and biosensors.

Experimental

1-(2-Cyanoethyl)pyrrole and iron(III) perchlorate hydrate were purchased from Aldrich Chemical Company, Inc. and used without further purification. Guaranteed reagent grade commercial potassium hydroxide, hydrochloric acid and acetonitrile were used without further purification.

Chemically oxidative polymerization of 1-(2-cyanoethyl)pyrrole was carried out as follows: 2.69 mg of iron(III) perchlorate was mixed in acetonitrile (50 ml) and added to 0.8 ml of 1-(2-cyanoethyl)pyrrole at room temperature. The precipitate was washed with a large amount of acetone, filtered and dried *in vacuo*.

The yield was determined by the following equation:

$$\text{yield}\,(\%) = \frac{\text{precipitate (g)}}{\text{1-(2-cyanoethyl)pyrrole used (g)}} \times 100$$

The hydrolysis of the cyano groups of PPy-Et-CN was carried out as follows: a suspension of 0.25 g of PPy-Et-CN in 100 ml of 5% potassium hydroxide solution was stirred at 50°C for 30 h, and acidified with hydrochloric acid.

I.r. spectra of the obtained polymers were measured using a Shimazu FTIR-8100M spectrophotometer.

The conductivity of these polymers was measured as follows: disc plates (the disc area was 1.33 cm^2 and the thickness was 0.71 mm) were made at a pressure of 500 kgf cm^{-2} by a hand press and gold was deposited on both sides of the disc plates as electrodes. Voltages from -2 to $+2$ V were applied between the two gold electrodes and current changes were measured by an Advantest TR8652 digital electrometer.

Results and discussion

Figure 1 shows the relationship between the yield of precipitate and reaction time. This result indicated that the precipitate formation was completed within 5 min and the yield levelled off at ~ 30%. Elemental analysis of the precipitate gave the following results: C, 53.5 wt%; H, 4.2 wt%; N, 17.9 wt%. The results suggested that PPy-Et-CN was synthesized successfully.

Figure 2a shows the i.r. spectrum of PPy-Et-CN obtained. The absorption peak in the region 2240–2280 cm^{-1} attributed to the $-\text{C}{\equiv}\text{N}$ stretching vibration is evidence that 1-(2-cyanoethyl)pyrrole was polymerized by the chemically oxidative process. *Figure 2b* shows the i.r. spectrum of hydrolysed polymer. Not only the

---

* To whom correspondence should be addressed

absorption peak of $-C{\equiv}N$ stretching vibration in the region 2240–2280 cm^{-1} but also that of C=O stretching vibration in the region 1650–1700 cm^{-1} was observed. This result suggests that part of the cyano groups on the surface of PPy-Et-CN powder were hydrolysed. The hydrolysed polymer (PPy-Et-COOH) contained cyano groups in some degree. The conversion of the cyano groups to carboxyl groups was determined to be ~ 14% by titration with sodium hydrogen carbonate[13].

In addition, the conductivity of PPy-Et-CN and PPy-Et-COOH was measured. *Figure 3* shows current–voltage (*I–V*) plots of both polymers. The conductivity of PPy-Et-CN and PPy-Et-COOH was calculated to be of the order of 10^{-7} and 10^{-12} S cm^{-1}, respectively. *I–V* plots of PPy-Et-CN showed the ohmic characteristics with the gold electrode. On the other hand, *I–V* plots of PPy-Et-COOH showed a slight hysteresis curve. It is considered that the carboxyl groups of PPy-Et-COOH induced dielectric polarization when the voltage was applied. Considering the conductivity of PPy-Et-COOH, this polymer exhibited insulating properties, because iron(III) perchlorate in the polymer was dedoped during the hydrolysis of the cyano groups. Iron(III) perchlorate can be regarded as a dopant in PPy-Et-COOH. *Figure 4* shows the i.r. spectra of iron(III) perchlorate. The absorption peak was observed in the region 1050–1200 cm^{-1}. This absorption peak was not observed in the case of PPy-Et-COOH but PPy-Et-CN (see *Figure 2*).

We have been investigating the application to electric devices and biosensors of these functional conductive polymers such as PPy-Et-CN and PPy-Et-COOH. For

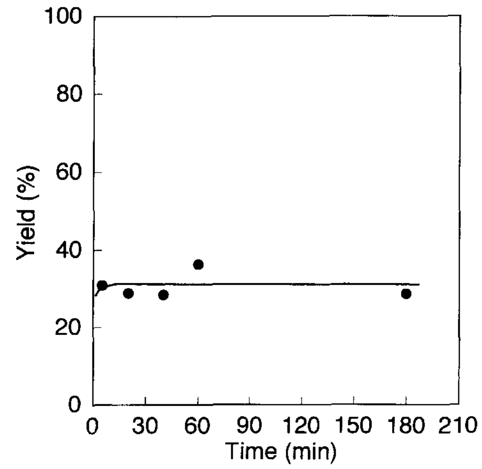

Figure 1 Relationship between reaction time and yield in the polymerization

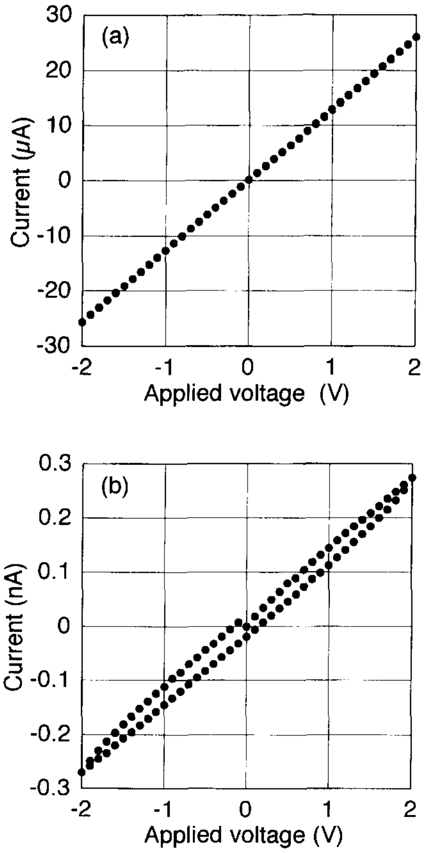

Figure 3 *I–V* plots of (a) poly[1-(2-cyanoethyl)pyrrole] and (b) the hydrolysed product of (a)

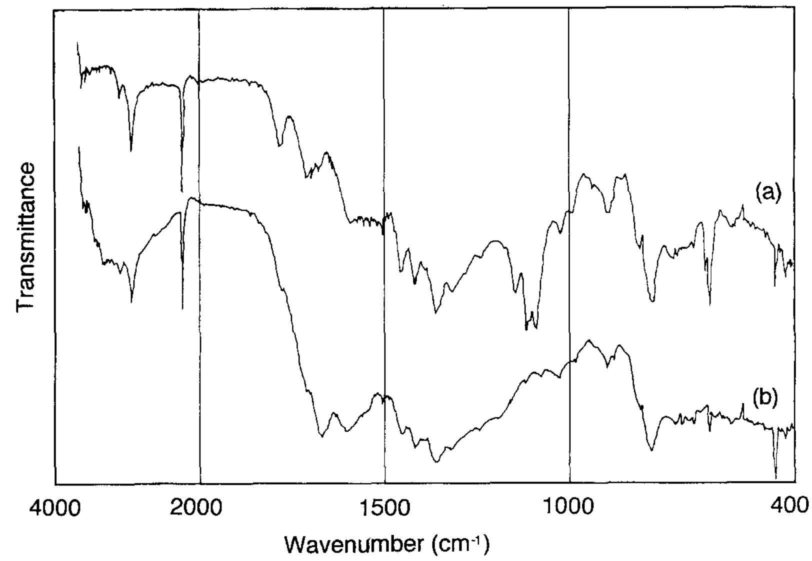

Figure 2 I.r. spectra of (a) poly[1-(2-cyanoethyl)pyrrole] and (b) the hydrolysed product of (a)

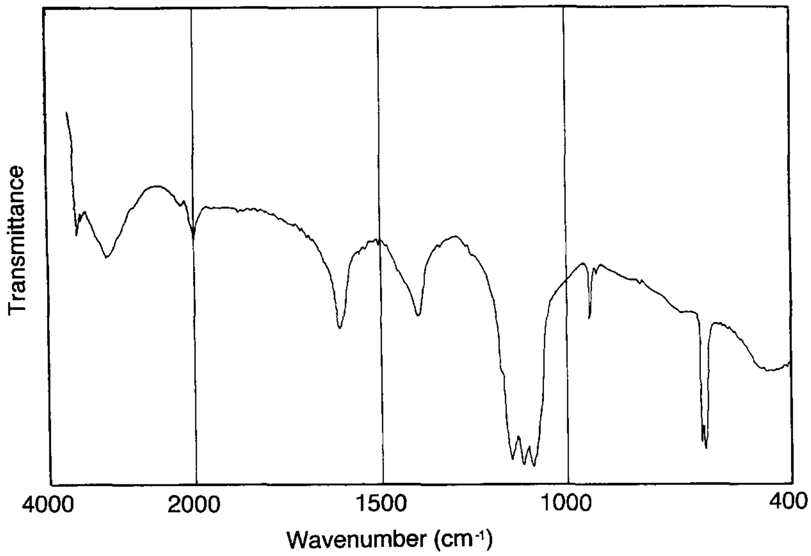

Figure 4 I.r. spectrum of iron(III) perchlorate

example, we have preliminarily tried the covalent binding of glucose oxidase to PPy-Et-COOH, and observed the specific activity of the immobilized enzyme. PPy-Et-COOH is a promising immobilization carrier of biomaterials.

Conclusions

PPy-Et-CN was synthesized by chemically oxidative polymerization. The yield of PPy-Et-CN was ~ 30% and the chemical structure was estimated from i.r. spectra. Cyano groups of PPy-Et-CN were easily hydrolysed to carboxyl groups and the conversion of PPy-Et-COOH was estimated to be ~ 14%. PPy-Et-CN had a conductivity of the order of 10^{-7} S cm^{-1} and indicated ohmic characteristics with the gold electrode. On the other hand, the conductivity of PPy-Et-COOH was 10^{-12} S cm^{-1} and the I–V plots indicated slight hysteresis characteristics.

References

1 Myers, R. E. *J. Electron. Mater.* 1986, **15**, 61
2 Armes, S. P. *Synth. Met.* 1987, **20**, 365
3 Bjorklund, R. B. *J. Chem. Soc., Faraday Trans. 1* 1987, **87**, 1507
4 Planche, M. F., Thiéblemont, J. C., Mazars, N. and Bidan, G. *J. Appl. Polym. Sci.* 1994, **52**, 1867
5 Ayad, M. M. *J. Appl. Polym. Sci.* 1994, **53**, 1331
6 Diaz, A. F., Kanazawa, K. K. and Gardini, G. P. *J. Chem. Soc. Chem. Commun.* 1979, **14**, 635
7 Asavapiriyanont, S., Chandler, G. K., Gunawardena, G. A. and Pletcher, D. *J. Electroanal. Chem.* 1984, **177**, 229
8 Foulds, N. C. and Lowe, C. R. *J. Chem. Soc., Faraday Trans. 1* 1986, **82**, 1259
9 Umaña, M. and Waller, J. *Anal. Chem.* 1986, **58**, 2979
10 Garnier, F., Youssoufi, H. K., Srivastava, P. and Yassar, A. *J. Am. Chem. Soc.* 1994, **116**, 8813
11 Degani, Y. and Heller, A. *J. Phys. Chem.* 1987, **91**, 1285
12 Wolowacz, S. E., Yon Hin, B. F. Y. and Lowe, C. R. *Anal. Chem.* 1992, **64**, 1541
13 Rivi, D. *Rubber Chem. Technol.* 1963, **36**, 729