Chemical polymerization of 3-methylpyrrole-4-carboxylic acid

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3-Methylpyrrole-4-carboxylic acid has been polymerized chemically. The polymer was compared with that prepared electrochemically using elemental analysis, *FT*i.r. and SEM.

(Keywords: chemical polymerization; electropolymerization; polymer characterization; self-doped conducting polymer; conducting polymer)

Introduction

Conducting polymers such as polypyrrole and polyaniline can be polymerized either electrochemically[1,2] or chemically[3,4]. The chemical polymerization of these two compounds is readily achieved since they are water soluble and are oxidized at relatively low anodic potentials. The chemical polymerization process is rapid and can be readily scaled up. In addition, the products can be bulk polymers or polymer coatings on other materials. In contrast, electropolymerization can only be used to deposit on electrode surfaces thus restricting the application areas to a limited range of materials.

3-Methylpyrrole-4-carboxylic acid (MPC) has been electrochemically synthesized in acetonitrile media[5–7]. The electropolymerization potential was found to be approximately +1.0 to +1.2 V, making chemical polymerization of MPC achievable. However, the monomer is not water soluble and the polymerization needs to be carried out in aqueous media to facilitate the use of water-soluble oxidants.

In this work, chemical polymerization of MPC using $FeCl_3$ has been investigated. The composition and structure of the chemically formed polymer have been compared with those of the electrochemically produced polymer.

Experimental

Reagents and materials. MPC was synthesized in this laboratory as described previously[3]. Tetra-n-butylammonium perchlorate (TBAP; Fluka) and *p*-toluene sulfonic acid (PTS; Aldrich) were used as obtained. The solvent used for chemical polymerization was 50% methanol and 50% deionized water. An aqueous 1.0 mol l^{-1} ferric chloride solution was prepared. A platinum plate (3 cm^2) was used as the substrate for electrodeposited polymers.

Synthesis. Chemical polymerization was carried out as follows: 0.40 g MPC and 0.64 g PTS or 0.40 g TBAP were placed in a 25 ml measuring cylinder. Methanol (5 ml) was then added to dissolve the compounds. A 5 ml sample of 1.0 mol l^{-1} $FeCl_3$ was then introduced into the measuring cylinder and the solution was stirred using a nitrogen stream for 48 h. During the reaction, methanol was added to compensate for evaporation of the solvent. The products were filtered using a Buchner funnel, washed with water and then with acetone several times before drying in air.

Electrochemical polymerization was performed as follows: 0.2 mol l^{-1} MPC and 0.2 mol l^{-1} TBAP or PTS solutions were prepared in CH_3CN. Using a stainless steel plate as the counter electrode, polymerization was carried out galvanostatically at a current density of 2–4 mA cm^{-2}. The polymer products were removed from the electrode and soaked in CH_3CN to remove residual monomer and electrolyte, and then dried in air.

Characterization. Elemental analysis was carried out by the Microanalytical Laboratory, Australian National University. Samples for *FT*i.r. were dissolved in 1 mol l^{-1} NaOH, coated on a KBr salt window (Activon) and dried with a hot-air dryer. *FT*i.r. spectra were obtained from a Bio-Rad FTS-7 spectrometer with an SPC-3200 workstation. Scanning electron micrographs (SEM) and energy dispersive X-ray (EDX) spectra were obtained from a Hitachi S-450 scanning electron microscope with a microtrace detector (United Science).

Results and discussion

To date, poly(3-methylpyrrole-4-carboxylic acid) (PMPC) has not been prepared using chemical methods. Consequently our initial studies were concerned with characterizing the material produced by using a chemical oxidant and comparing it to that produced electrochemically.

The use of methanol and water as solvents enabled the dissolution of $FeCl_3$ as well as MPC. Chemical polymerization was performed in media which contained monomer, oxidant and PTS or TBAP. It was found that the presence of PTS improved the solubility of the monomer, which has low solubility in water[4]. It was also found that the composition of the polymer varied depending on the method of preparation, as indicated by elemental analysis data (*Table 1*). Counterions were

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Table 1 Elemental analysis of chemically and electrochemically polymerized PMPC

Experiment[a]	Medium	Analysis (%)[b]				
		C	H	N	Cl	S
1	0.20 mol l^{-1} MPC 0.20 mol l^{-1} PTS in CH_3CN	57.15 (6.6)	4.67 (6.4)	10.17 (1.0)	–	1.90 (0.08)
2	0.20 mol l^{-1} MPC 0.20 mol l^{-1} TBAP in CH_3CN	46.9 (5.4)	3.6 4.9	9.5 (1.0)	2.5 (0.1)	–
3	0.32 mol l^{-1} MPC 0.33 mol l^{-1} PTS 0.50 mol l^{-1} $FeCl_3$ in 50% H_2O+ 50% MeOH	53.9 (6.2)	4.5 (6.2)	10.9 (1.0)	2.4 (0.09)	0.7 (0.003)
4	0.32 mol l^{-1} MPC 0.11 mol l^{-1} TBAP 0.50 mol l^{-1} $FeCl_3$ in 50% H_2O+ 50% MeOH	47.7 (5.5)	4.4 (6.0)	10.0 (1.0)	1.8 (0.07)	–

[a] 1 and 2, electrochemical polymerization; 3 and 4, chemical polymerization, as detailed in the Experimental section
[b] Figures in parentheses are relative mole ratio to N

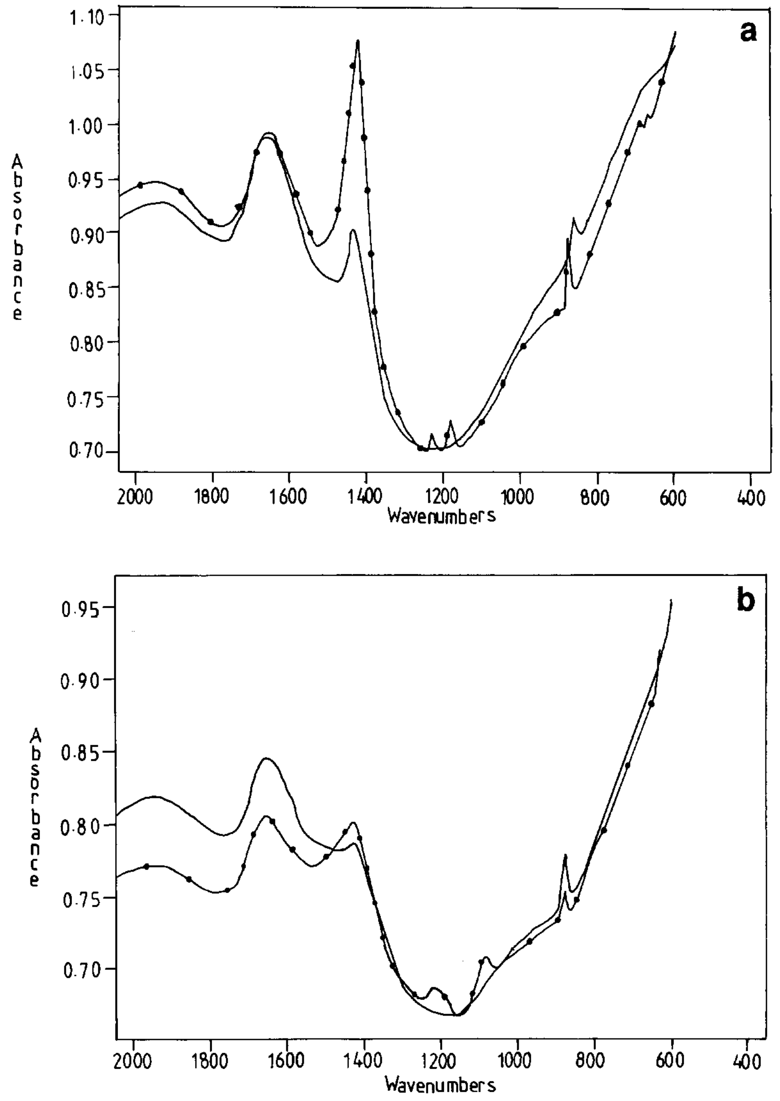

Figure 1 *FT*i.r. spectra of PMPC polymerized in a solution with (a) PTS and (b) TBAP: ●-●-●, by electrochemical polymerization; ——, by chemical polymerization

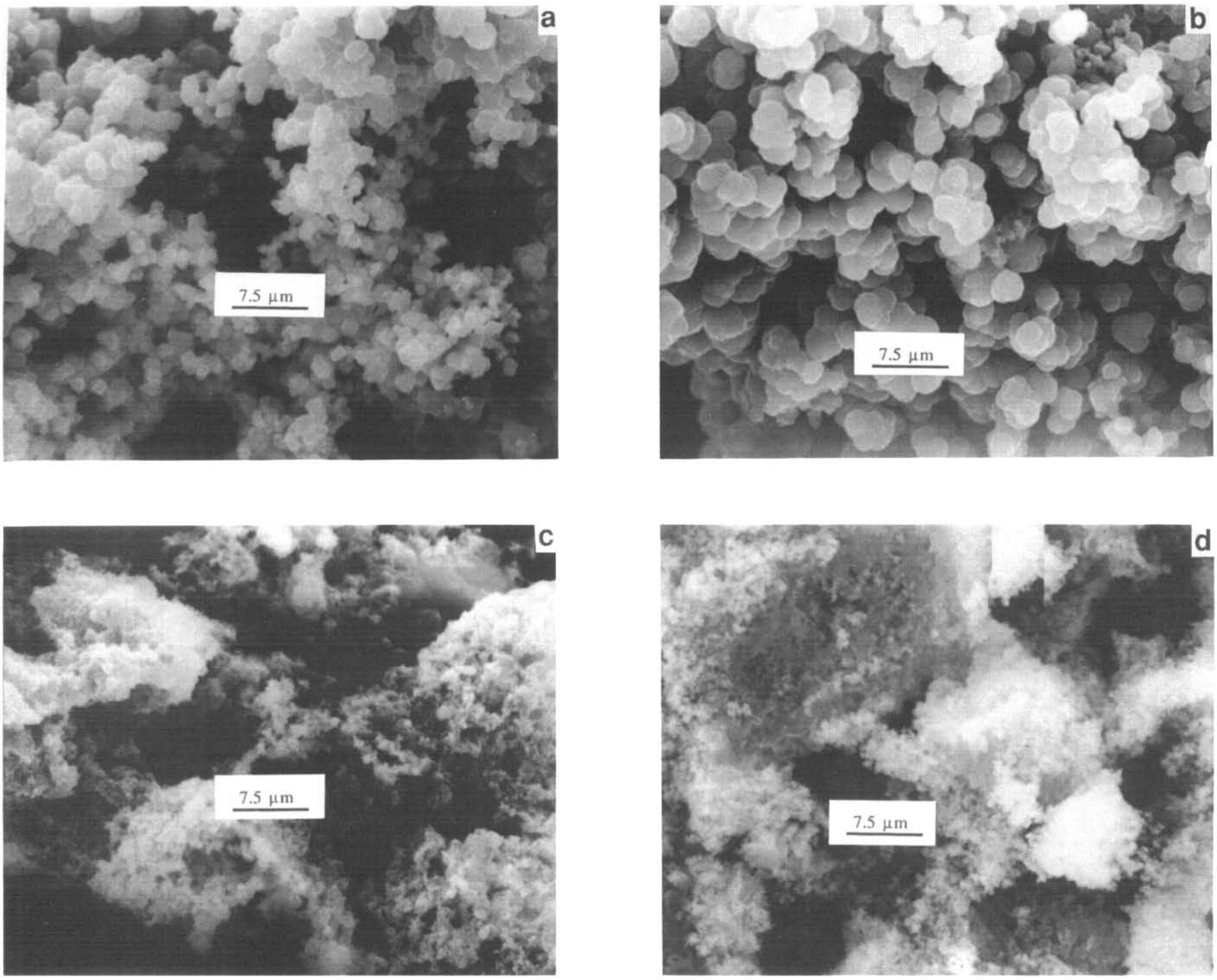

Figure 2 Scanning electron micrographs of PMPC. Experiment number (corresponding to *Table 1*): (a) 1; (b) 2; (c) 3; (d) 4

incorporated during both electrochemical and chemical polymerization. With electropolymerization only the electrolyte anion was available to be incorporated, while with chemical polymerization the main counterion incorporated from a Cl^- and PTS^- mixture was Cl^-. In all cases the monomer unit to counterion mole ratios were very high (10–14). This indicated that the polymer doping by counterions was low as compared with the ratio of 2–6 monomer units to one counterion observed with polypyrrole[5]. This implies that self-doping of the PMPC by the –COOH groups at the 4-position of the pyrrole ring probably occurs. All the prepared polymers appeared black and they dissolved in $1\,mol\,l^{-1}$ NaOH to form a green solution.

*FT*i.r. spectra are depicted in *Figures 1a* and *1b*. Counterion peaks were not detected on chemically formed polymer but were observed from electropolymerized PMPC. Thus for PMPC/PTS, $-SO_3$ symmetric and asymmetric stretching vibration and aromatic –C=C– stretching vibration were found at 1186, 1234 and $1573\,cm^{-1}$, respectively. These peaks corresponded to free PTS peaks at 1186, 1214 and $1650\,cm^{-1}$, respectively. ClO_4^- gave a peak at $1097\,cm^{-1}$ but this split into four additional peaks in $PMPC/ClO_4$. Characteristic polymer peaks appeared at 865, 1443, 1650 and $1950\,cm^{-1}$. The peak at $1443\,cm^{-1}$ was also observed with the monomer only, indicating that it was due to the pyrrole ring (C=C and C=N in-plane vibration). The broad peak at $1650\,cm^{-1}$ may be due to carboxylic salt asymmetric stretching vibration, which was also found for the monomer only. The peak at $865\,cm^{-1}$ did not appear in the monomer spectrum.

The SEM micrographs showed that different physical structures were obtained using electrochemical and chemical polymerization processes (*Figure 2*). The polymers formed electrochemically were more crystalline. This indicated three-dimensional growth of the polymer during electropolymerization. EDX analysis further confirmed that Cl^- was incorporated during chemical polymerization.

Conclusions

During chemical polymerization of MPC the main counterion incorporated was Cl^-. Structural differences in the counterions were observed by using the *FT*i.r. technique. The chemically formed polymers showed different physical structure from the corresponding electrosynthesized ones. PMPC prepared by chemical as well as electrochemical methods are self-doped by –COOH at the 4-position of the pyrrole ring.

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